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In 1901, Mary C. Weston and Ambrose had been
both of whom provided wonderful inspiration.

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is a 1:1 Cu:ligand complex (blue) known for DMSO in which they are observed. Finally, molecular weight and conductivity results suggest that in DMSO enhanced partial ionic dissociation of the complexes. The free ligand was never synthesized directly nor was it isolated from the complex as a part of numerous attempts to do so. The differences between these closely related macrocyclic complexes in the aqueous susceptibility and ultraviolet-visible spectra are interpreted in terms of a slight pestering of (1). The steric interaction is inferred from a consideration of the Frank-Condon Molecular Model.

A related ligand, 1,3,13,14-tetraazacycl-3,4,13,14,18-hexamethylcyclo[15.5.1.1^{3,11}.1^{13,15}]siloxane-1 (19), 3,4,8,8,14(CH₃),-11,13,15,15-dioxane, was prepared as its nickel(III)oxalate complex XIX and partially characterized by its elemental analysis and infrared and magnetic susceptibility measurements. The room temperature magnetic moment is 1.65 B.M. no assignment was made to explain the anomalous value, but due to the similarity of the complex to XI and XII, it may be arising from the same phenomenon.

A series of $\text{Ni}(\text{II})$ and $\text{Zn}(\text{II})$ complexes with 2,2',2''-terpyridines (TTPAS) were prepared and characterized. The ligand, which occupies three bonding sites, leaves a vacant open site(s). The fourth coordination site is occupied by the anion of the metal salt used in the preparation to give a neutral, monomeric complex. Based upon the disappearance of the ^{57}Fe complexes prepared, the complexes are

analysis of 10 polymers, glass polymers. The samples were characterized by infrared, ultraviolet and viscometric methods. Molecular weights, molecular viscosities, and molecular weights per monomer, were determined. It was also demonstrated that the polymers, could serve as useful starting material for the preparation of copolymers.

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I
INTRODUCTION

A macrocyclic complex is one in which the metal ion is enclosed by a ligand which is itself a closed ring. Coordination complexes in which metal ion cations are bound by organic macrocyclic ligands have been known for over sixty years, but only during the past decade have a significant number of these new complexes been designed, prepared and investigated. The first examples to be investigated were the naturally occurring porphyrins or corrin ring types II and III, p. 178. Several reviews¹⁻⁴ have summarized the chemistry of these important complexes.

In addition to being involved in a variety of catalytic and enzymatic reactions,⁵ macrocyclic complexes are known to function in at least three additional major biological activities. Metal complexes are involved in material transfer such as oxygen transport by hemoglobin, in material storage such as that of iron by ferritin and in energy transfer as performed by the chlorophyll systems. More workers have also proposed that a macrocyclic function is involved in natural nitrogen fixation.⁶ Additional review articles addressing various aspects of the coordination chemistry of macrocyclic ligands reflect the increased attention this class of compounds has attracted.⁷⁻¹¹ In fact, the entire Volume 189 of Advances

the investigation of the biological involvement of these systems, and in which are no chemical complexes.

The investigation of biological systems in biological processes leads appeal to the investigation of the understanding of life has always been one of man's greatest aspirations. Thus, knowledge of the properties and behavior of macroyclic complexes is desirable for the understanding in any impact to biological behavior. Such knowledge should also contribute to the preparation of synthetic systems useful for the treatment or study of biological irregularities once they are outlined. Functional biological systems form any macrocyclic coordination are extremely complex. As a result, attempts to separate and identify the various influences due to the natural macrocycles are often difficult or inconclusive. This dilemma can be partially circumvented by the use of synthetic models. Because of their relative simplicity, synthetic models sometimes allow the identification of a single crucial factor or among a large number of possibilities. Recently, separate articles by Bush,¹⁸ Schubert¹⁹ and Klier²⁰ exemplify how research on synthetic systems can provide new approaches to understanding biological ones. Although a fairly limited amount of research has been reported to date, for the above and more purely chemical systems, the number of synthetic macrocyclic systems continues to increase, leading to the expectation of a wealth of fruitful data.

Two generalizations which have distinguished macrocycles from other systems are their stability and inertness.

These 14 reactions, in which the metal is in a thermal decomposition and undergoes a variety of ligand substitutions. Curcio noted these characteristics in a review formed by the reaction of triethylenediamine with $\text{Co}(\text{H}_2\text{O})_6^{3+}$ with the sodium anhydrous acetate.¹² The proposed ligature was disrupted when the stability to hydrolysis was noted and compared to other seemingly similar complexes.¹³ The complex produced was correctly described as a quadridentate macrocycle which constituted the first new series of complexes of this class to be developed synthetically since the phthalocyanines.¹⁴ Curcio's study represented a rather cautious preparation of a macrocyclic complex as has been the purpose of later investigations to synthetically design and prepare synthetic macrocyclic complexes.

Most macrocyclic ligands isolated or synthesized thus far are tetradentate and approximately planar. The donor sites must be positioned regularly around the ligand so that the individual chelate rings (including the metal center) have five, six, or in rare instances, seven atoms (IIC, p. 138). Complexes have been prepared with first row transition metal centers in their common oxidation states using ligands containing 12-14 atoms in the primary chelates and having all nitrogen donor sites.¹⁵⁻¹⁷ Some macrocycles are known in which some or all of the donor functions are copper or sulfur atoms.¹⁸⁻²¹ The optimum ring size is surely a function of the "hole" size which the metal must fit. Thus larger metal atoms (second and third row transition elements) as ligands

many atoms (including sulfur, phosphorus, or arsenic) are likely to require a larger ring. Recent work in which all sulfur donors were used instead of nitrogen demonstrated that the minimum number of atoms in the ring must be greater than 12 atoms in order to demonstrate first row transition metals.¹¹ Smaller rings may still function as chelating agents but must assume a folded (non-planar) form and thus do not circumscribe the metal ion.¹² The literature also contains examples of perfluorates, azidoazides, and higher polydentate macrocycles.¹³⁻¹⁶ However, due to the exhibited biological importance of macrocyclic macrocycles, the emphasis here will be focused on those systems which circumscribe the metal at approximately co-planar positions.

Naturally occurring macrocyclic complexes such as chlorophyll, hemocyanin and vitamin B₁₂ are all characterized by a high degree of coordination to the organic chelate surrounding the metal ion. Many of the highly conjugated natural systems such as porphyrin chelates satisfy the Hückel criterion $4n + 2$ π -electrons allowing for aromaticity in the organic ring. In isolated organic molecules, the aromatic character arising from an $4n + 2$ π -electron system is well known to confer stability to the system,¹⁷ and this may also be present in glasses.

Since stability can be imparted to the liquid-metal bond a coordination of a donor site to the central metal ion certainly requirements are met.¹⁸ The essential requirement that 1) the metal orbital electrons in the d_{xy} and d_{yz}

orbital (labeled) σ bond given is further seen that the orbital interaction is coordinated in the xy plane and to the ligand contains \underline{g}_i -antibonding molecular orbitals of proper symmetry in which the contribution of the donor metal atom is finite. These two criteria allow back donation of the d -electrons from the metal to the \underline{g}_i -antibonding orbitals of the ligand resulting, in essence, as a double bond character of the metal-ligand bond; thus the metal-donor interaction is enhanced. The synergic effect¹¹ is operative and serves to strengthen the bonding between the metal and the ligand to an even greater extent. This effect may be viewed in the following manner- as electron density is donated from the metal d_{xz} and/or d_{yz} orbitals into the ligand \underline{g}_i -antibonding orbitals, the metal becomes more able to accept sigma electron density from the ligand. Furthermore, as a consequence of the ligand sigma donation the ligand is more able to accept \underline{g}_i -electron density. Thus, mutual enhancement of the donation and acceptance of electron density occurs between the metal and ligand. The formation of the double bond is apparently responsible for the unexpected stability of carbon monoxide¹² complexes and for the existence of molecular nitrogen¹³ complexes since the sigma donation of these two ligands is extremely weak when they are bound to the metal in an end-on fashion. This rationalization is consistent with a reduction of the stretching frequencies of the C-O and N-N bonds upon coordination which indicates the donation of electron density into the antibonding \underline{g}_σ system of the ligands, hence the

ligands which good character of the metal-ligand bond. Thus, it is apparent that π -backbonding may be good character can be expected in metal-ligand bonds. The π -backbonding frequently occurring in natural systems meets the criteria listed above and, indeed, experiments have shown that there appears to be considerable stabilization of the metal-ligand bond through partial double bond formation.¹⁰

Another factor leading to enhance the stability of metacyclic complexes is the chelate effect. That is, a metal chelate complex is more stable than a related complex containing only unidentate ligands.¹¹ This effect is commonly divided into an enthalpy and an entropy contribution. The enthalpy consideration arises from the greater crystal field splitting produced by the multidentate ligand.¹² The amount of the enthalpy contribution is not entirely agreed upon, but it is possible that when double bonding is present in the metal-ligand interaction, the stability may partially arise from the same crystal field splitting caused by the interaction of the t_{2g} orbitals of the metal in these systems.¹³ In a molecular orbital diagram for an octahedrally coordinated system, the difference in energy between the t_{2g} and e_g orbitals of the metal is increased when the ligand orbitals of g_u symmetry are unfilled and higher in energy than the t_{2g} orbitals contained on the metal. This situation is likely to be realized in most chelates involving donor molecules, and thus there should be an increased crystal field stabilization accounting for part of the enthalpy effect.

... a smaller number of donor ligands than a complex is formed from a larger number of species than from a small number, complexes of bidentate ligands are entropically preferred over those of monodentate ligands.²² Regardless of the explanation chosen, ²² it is fact they may both be operative, there is a stabilizing of a chelate system relative to a similar, monodentate system.

One other way of viewing the entropy effect may be based again on probability grounds. In a chelating ligand, if one of the donors dissociates from the metal center, it is likely to be held in close proximity of the metal ion since one or more of the additional donors will hold the chelate molecule to the metal. This allows the dissociated donor to later become reassociated whereas for a monodentate ligand, the remaining complex and ligand are become separated upon dissociation. Following this rationale, the planarity forced on the basic organic ring of conjugated macrocyclic rigidly holds a dissociated donor in the vicinity of the metal until recoordination takes place. Since the basic ligand is almost infinitely about the metal ion, it is possible that a donor in the plane of the molecule can rarely be defined as truly dissociated as long as one or more of the other donor atoms remain coordinated. Most likely, a combination of all the above effects result in the exceptional stability and inertness of macrocyclic complexes.


With the size and the polyfunctionality of the primary organic ring structure complicate synthesis routes for the

preparation of the ligand. Consideration is also given to the relative positions of the donor atoms with respect to each other, to the central metal ion (or other component of the ring. Steric interactions between ring substituents may either permit or prevent folding of the basic ligand ring, thus controlling the possible modes of coordination. The positions of additional ligands in the complex may be affected in turn by the mode of coordination, or conversely, their presence may affect the mode of coordination for the basic ring.

The design of chelating agents also requires awareness of the steric effects of conjugation in the ring system. A number of the synthetic macrocyclics, and, indeed many of the naturally occurring ones, exhibit a high degree of conjugation within the basic ring, resulting in extensive electron delocalization. The additional stability present as a result of the bonding was discussed previously. Here, structural consideration of the conjugation will be viewed. Conformationally, the most drastic effect of conjugation is the distorting of a strictly planar ligand system. This distortion is reinforced by the geometrical requirement of the metal which dictates that the four donor atoms in the xy plane of the complex be capable of assuming an essentially planar array, although this alone does not impose any restrictions on how the ligand donors are connected together.

Remembering that the geometries of macrocyclic complexes arise mainly from the central skeleton of the complex, and

and the peripheral constituents, and keeping the previously discussed requirements in mind, an attempt to design and synthesize macrocyclic ligands was begun. In any such endeavor, several important decisions must be made. One choice to make is the type of donor atom to use. These can be incorporated into the system via a number of different functional groups. Oxygen can be used as a donor when contained in methoxylate, phenoxylate, methoxymethyl, amidate, S-amide or ether groups. Sulphur atoms can be substituted for some of the oxygen donor atoms. Nitrogen can be utilized through primary, secondary and tertiary amine, amine, amine or amide groups. These various functional groups provide donors with a range of affinities for a given metal.¹² Furthermore, they provide some conformational influences due to the specific directional nature of the coordinating lone pair of electrons on the donor atom.⁶ As stated previously, the main interest was directed towards biological systems and a vast number of these systems involve all nitrogen donors in the plane. In addition, these complexes have a high degree of conjugation which necessitates incorporating the nitrogen donors as values if conjugation is to be preserved. The task at hand, then, was to find appropriate molecules to form the desired basic ring when reacted. In essence, one has available the whole of organic chemistry to facilitate the linking process. Practically, however, one has a much more limited repertoire from which to choose. One of the logical approaches appeared to be the reaction of formaldehyde with amines which joins

the two groups via a methylene group. Other alternative synthetic routes are the reactions of nitriles with amines and carbonyls with amines. The latter reaction is by far the most commonly organized preparative route in the literature. Also, it seemed most desirable for this work since the reaction yields a condensation product with a structure  (Smith 1966 or 1968). These products are well characterized and most of the efforts reported herein were directed towards this reaction path.

Such "paper chemistry" needed to be conducted to choose appropriate starting materials that would fit into the desired pattern of a conjugated linear ring containing the four nitrogen donors. Many possible reactants such as bisacetyl and ethylenediamine have two or more reactive sites. Having two reactive sites per molecule may yield a host of alternative reactions (e.g., polymerization) other than the desired cyclization process.

In the event that polymerization could not be controlled relative to cyclization, it would be necessary to consider an alternate synthetic design. A logical change would be to choose starting materials in which the reactivity of the two functional groups contained in a given molecule differ significantly, thus potentially eliminating the polymerization problem. This could involve unsymmetrical molecules such as pyrazaldehyde (IVr, p. 142) and phenylglyoxal (IVS, p. 142).

Again, if the desired cyclization was not accomplished, a reasonable, but different approach which could be invoked

involves the use of protective groups, e.g., acetals in place of a carbonyl group on one side of the previously bifunctional reactants in an effort to retard linear polymerization. In this manner it should be possible to partially construct the ring and then to introduce the metal to hydrolyze the acetal function allowing the final cyclization to occur in the presence of the metal which should also orient the reactants properly (vide infra).

Most of the synthetic macrocycles reported have been prepared in the presence of metal ions which might aided the synthesis by improving the yield or was absolutely essential for product formation. However, the synthesis of at least one macrocycle has been reported that was unexpectedly straightforward without the aid of any metal.⁴¹ The improved yield in the case of metal addition is a consequence of one of the two metal ion effects collectively referred to as coordination template effect.⁴ It is broken down into at least two types of instances. If the metal is acting in a directive capacity, controlling the steric course of a sequence of stepwise reactions, the process is considered to be a kinetic template effect. The principal factor would then be to organize the reactants by orienting them so that the functional groups are in the immediate vicinity of each other allowing the condensation to proceed to the desired product. The metal ion may also function in yet a different manner to increase the yield of desired products. In this second case, the metal is used to perturb an equilibrium in the aqueous system. For example, it may selectively remove some intermediates in a

sequence of chemical products. This area of activity has been labeled the thermodynamic template effect. In other terms, the latter effect is in reality an alteration of the equilibrium processes with respect to the usual functions of the metal and ligand. In reading, this would imply that there is no effect on the organic mechanisms that were operative other than a simple halting of a sequence at some point in the overall process. However, it appears that a metal merely alters the thermodynamic effect in macrocycle production without also utilizing the kinetic effect because the intermediate coordination products would coordinate as well as the final product. If chelation occurs at any point in the sequence of condensations other than the final completed cyclic product, then the kinetic effect must be operative.

When the kinetic template effect operates most efficiently, the orientation of the reactants is aided by a particular structural feature of one or more of the reacting molecules. An example of such a structural feature is the presence of a donor atom in addition to, and located between, the reacting groups on the molecule during the macrocyclization process. That the presence of this structural feature is important if not absolutely necessary can be seen from the proposed mechanism of the Schiff base formation, i.e., the amino group which functions as a nucleophile in the condensation process cannot so function if the lone pair of electrons is involved in the coordinate bond formation with the metal. Thus, the amino function must be dissociated from the metal for the

coordination is weak; i.e., labile, the molecule containing the active function possesses an additional coordinated atom, the molecule remains bonded to the metal during the dissociation of the active function and its subsequent substitution. Substitution of the newly formed union is highly probable in view of the proximity of the newly formed ligand union donor, on the basis of the aforementioned rationale. It would appear that any basic approach to the design and synthesis of macrocyclic ligands would be more advantageous if the kinetic template effect were incorporated into the reaction scheme.

It was the objective of this investigation to prepare (Va, Vb and Vc, pp. 14-43) by using the template effect. Several of the approaches discussed above were to be incorporated into these preparations. Indeed, 4,13-dimethyl-7,11-octadecane-1,13-dithiolane(2,8)[1,2,5,13] tetrasubstituted-*desferri*-nickel(II)chloride,* abbreviated as [Ni(makemakay)Cl₂] (Va) was to be attempted by three different procedures. The first preparation would involve the addition of 2,2'-diamino-azobenzene (DABAM, VII) to a solution of nickel(II) and 2,8-diaminopyridine (DAP, VIII). This method would utilize the kinetic template effect to orient the reacting species in the correct manner to yield the desired macrocycle (Va) since both reactants fulfill the criteria listed above. A second procedure was developed to use the thermodynamic template effect. Here the metal would be added to a solution

* IUPAC names provided by Kurt L. Lonsing, Chemical Abstracts Service.

complexed the diene and the pyridine diene presumably already undergoing reaction. It was anticipated that the metal would remove the desired cyclic product or partially cyclized product from the other possible organic compounds. If it was observed that the diene above was capable of forming a well defined complex with the metal, a third procedure would be used. It would involve isolation of the metal-ene complex and using stoichiometric amounts of the preferred enone and the diene to condense into the desired macrocycle. A description of the main complexes will also be incorporated into this dissertation because of their relevance to the macrocyclic synthesis.

Attempts to generate an analog of the diene would be attractive in order to evaluate the impact of strain present in the ligand if a planar configuration were taken. The strain might be caused by the methyl groups of the pyridine moiety, and preparation of an analog absent of the two methyl groups should have relieved the steric hindrance. Framework Molecular Models would be used to determine the type and amount of strain present in the system. It was our desire to then prepare 7,11-nitrile-11 β -diene[4,6] [1,2,3,12]-tetramacrocyclopentamethylene[12] chloride, (21-macrocyclopent-1,4-diene) (PM) by the condensation of octane (VII) with 2,6-pyridine-dicarboxaldehyde (PMO, II). Conditions similar to those used in the [6]macrocyclopent[12] synthesis would be followed. Since the greater reactivity of the aldehyde functional group would allow a larger variety of reactions compared to the ketone grouping, this may lead to the production of a larger variety

of organic substances. Therefore, studying the behavior of the log in the pure state might prove to be much more difficult.

the third macrocycle, 2,3,11,14-tetraazaporphyrin-2,4,12,13,15,16-hexamethyroporphyrin (13, 1,1) (Scheme 1) (13, 2,4,6,8,10(10), 11,12-13,17-decamethylchlorophyllide,^{9,10} [Mg]tetraaminoPChl.) which would be prepared by the condensation of 2,6-diacetylpyridinealdolhydrazones (VIIa) with 2,4-diacetylpyridine (VIII). These reactions were chosen to again use the kinetic template effect if possible. This proposed product is structurally interesting in that it contains 14 atoms in the basic organic ring allowing for two 3-member and two 4-member chelate rings. This appears to be the optimum size for the first row transition metals.^{1,2} However, many of the naturally occurring macrocyclic complexes such as haemoglobin and chlorophyll contain only six-member chelate rings. The organic ring also possesses a high degree of unsaturation and, in fact, contains $4n + 2$ atoms which satisfies the Hückel criterion for aromaticity, if the deformation effect is neglected. An interesting feature of this synthetic system is that the only valence bond structures which can be written with alternating double and single bonds involve formal charge development. This peculiarity is due to the pyridine portion where there are normally two adjacent "single" bonds. The two previously mentioned macrocycles, [Ni]tetraaminoPChl. and [Mg]tetraaminoPChl., also have a high degree of conjugated unsaturation but are non-alternate systems. Valence bond structures with alternating double and single bonds cannot be written because the basic ring contains 11 atoms. Furthermore, the $4n + 2$ Hückel rule is not satisfied.

Attempts will be made to prepare the aldehyde analog (VII) of the squarone macrocycle in the hope of preparing an analog to the (tridentate)antennic(II,1) free of the steric strain possibly caused by the methyl groups.

Other macrocyclic structures are contemplated in an effort to use the kinetic template effect during synthesis. Various molecules were chosen which would most likely have the coordination properties required for the above effect to operate. These macrocycles will be investigated in an attempt to alter the structural configurations, reactivities and physical characteristics, such as solubility, of the complexes.

To summarize, the objectives of this research include: (I) a description of the synthesis and characterization of (tridentate)antennic(II,1), (tridentate)antennic(II,2) and (tridentate)antennic(II,3), (II) a description of the synthesis and characterization of a new series of macrocyclic complexes and (III) a description of additional synthetic approaches to the preparation of macrocyclic complexes.

CHAPTER II

RESULTS AND DISCUSSION

The preparation and characterizations of the complexes studied are presented in the following order. $[\text{Pt}(\text{acac})_2\text{mer}(\text{Cl})_2]$ in Section A, $[\text{Ni}(\text{acac})_2\text{mer}(\text{Cl})_2]$ in Section B, $[\text{Ni}(\text{acac})_2\text{mer}(\text{Cl})_2]$ in Section C and $[\text{Ni}(\text{acac})_2\text{mer}(\text{Cl})_2]$ in Section D. Section E discusses the results of the early synthetic routes pursued and the rationale used in the preparative attempts. The material in the final section is presented in approximate chronological order to emphasize the successive investigations that were conducted and the alterations which were employed in an effort to obtain the desired macrocycle. The author believes that the material of the final section would be of sufficient experimental interest to future investigators to warrant its inclusion. While most of the results were of a negative nature, the entire line of problems enumerated may provide considerable insight into and to others attending further pursuit of this or related work.

All of the structures of the various complexes and starting materials are presented in Appendix I rather than through the text because of the frequent references made to some of them, thus facilitating the location of a particular structure when needed.

2. Macrocyclic Ligands (2.1)

The preparation of the macrocyclic complex [Ni(tetraphenylporphyrin)]₂ (9a), was not a trivial synthetic problem. Indeed it involved a number of unsuccessful attempts before isolation of the desired system. The strategy developed for the synthesis of this complex arose from considerations of the literature available on other synthetic systems. First of all, it was noted that a vast majority of the successful syntheses incorporated into the macrocyclic ring a molecule containing a donor atom in addition to the reacting groups that were used to join the precursor segments into the cyclic complex (vide infra). Secondly, examining that the template effect is realized, there seemed to be two major patterns emerging in terms of the sequence of introducing reactants. The first pattern is what will be termed a "template reaction". In this procedure, the metal ion and at least one of the components used to build the ligand ring are placed in the same solution and then the final portion of the ligand components is added. The other sequence is one in which the components for assembling the macrocyclic ligand are introduced together in solution, and are allowed to be in contact for a short period of time (several minutes), after which the metal ion is introduced. This latter scheme will be termed the "delay reaction". It is tempting to postulate that the reaction in the former sequence is operating via the kinetic effect while the latter is functioning through the thermodynamic effect. The decision

to use both addition mechanisms was based on the observation that, indeed, different effects are operative; however, it may well be that the mechanisms are identical in some instances. To elucidate the mechanisms of these reactions requires a detailed kinetic study, but, this was not an objective of these investigations.

The molecules chosen to build the new macrocycle were **20HAB** (**VI**), a diamine composed with an amine function as the "anchor" group and **40HAB** (**VIII**), a diquinoxyl composed with a pyridine donor as the "anchor" group. Each of these molecules possesses an "anchor" donor atom not a part of the reacting groups. A stoichiometric amount of the metal ion was used to give a 1:1 ratio of metal to potentially completed macrocycle. Following the rationale presented in Section 2 (vide infra), the orientation of these two molecules by the metal ion would be facilitated by their structural features. **20HAB** has the capability of providing one of the amine nitrogen lone pairs to hold the molecule to the metal ion while reaction is occurring at either of the amine groups. Noting the relatively weak donor strength of an amine nitrogen,¹⁷ it seems likely that the molecule would require more than the lone amine nitrogen to be coordinated to maintain the proper orientation. However, when one considers the improbability of having both amine groups dissociated and reacting simultaneously, it seems probable that, at any instant, there would be one of the amine groups coordinated in addition to the amine group. In a similar manner, the orientation of the quinoxaline DAP (**VIII**) is probably

aided by coordination of the pyridine nitrogen. Provided three positions in the metal ion plane are occupied by COBALT (VII), the coordination of H_2O (VIII) in the appropriate location, trans to the two functions of COBALT, would orient the carbonyl groups in close proximity to the amino groups with which they must react to form the macrocycle (IX). Given the structural features of these reactants, a functioning of the metal via either of the template schemes seemed quite plausible.

It is significant to note that the same macrocyclic complex is generated by both of the procedures described earlier. The "template reaction" involved the slow addition of an ethereal solution of the amino ligand (VII) into a refluxing ethereal solution of $\text{Ni}(\text{Cl})_2$ and the pyridine dibromide (VIII). The yellow-green solution changed to purple on addition of the amino ligand and then gradually changed to a red-brown. The product was then precipitated (vide infra) by ethyl ether and collected after seven to twelve hours of reaction. In the "delay reaction" strategy, the sequence of addition was changed so that the metal was added as a solid, hydrated salt to the previously mixed and refluxing COBALT (VII) and H_2O (VIII). Using the same total reaction times, the same color change as was noted in the "template reaction" occurred and the same product was formed. A few drops of hydrochloric acid (or, for the sake of generality, the conjugate acid of the amine contained in the $\text{Ni}(\text{Cl})_2$ salt) was added to the reaction mixture to catalyze the formation of the imine bond. This procedure was adopted because Schiff base condensations are

catalyzed by acid,¹³ and the use of acid catalysis has been reported for other macrocyclic syntheses.¹⁴ In fact, the addition of three equivalents appears to provide the best acid catalysis initially; however, the decision to add acid was made prior to the stoichiometric determination of the macrocyclic nickel complex (XII) (vide infra). With Ni(III), the OCOMeS functions as a tridentate ligand and simultaneously leaves one amine proton. The complex is characterized by an intense purple color which is observed immediately upon the addition of the ligand and the metal ion. The development of this color upon the first addition of the complex (VII) to the Ni(III) and DAP (VIII) solution or upon the addition of the solid metal salt to a solution containing the OCOMeS and DAP suggests immediate and complex formation. As a result, a small amount of acid is generated which contributes to the total acidity and this alone may have been sufficient to catalyze the nickel ion coordination. This hypothesis was not tested, however. The amount of acid added did surpass the amount released by the formation of the macro complex since fairly dilute working conditions were employed. If the acidity level becomes too high, the amine groups may be rendered unreactive due to the loss of mesophilizing or protonation. However, no difficulties arose by the use of up to ten drops of concentrated acid in a total reaction volume of approximately 120 ml ethanol. It may well be that proton catalysis would not be necessary when metal ions are present since coordination of the carbonyl oxygen to the metal would

generate a formal positive charge on the carbon bonded to the oxygen to facilitate a nucleophilic attack, just as happens when the oxygen becomes protonated.

A third method was developed and employed in the preparation of $(\text{Ph}(\text{acac})\text{Ni}(\text{II}))$ after elucidation of the composition of the $(\text{nickel}(\text{II})\text{-acil})$ complex (XII). The macrocyclic product (xvi) was obtained by addition of an ethanolic solution of $\text{EtP}(\text{VII})$ to a refluxing ethanolic suspension of the nickel(II) ac aceton (XII) . The product was subsequently collected as before after displaying similar reaction times and observing the color change from purple to red-brown. The products of all three preparations were identical in texture, color, spectral properties and analyses.

Because of the great similarity in the observations noted during the different syntheses, it is entirely reasonable to conclude that all three are proceeding via the same pathway. Recalling that the metal center may alter the course of reaction by collecting the organic ligands in its coordination sphere prior to the condensation steps (kinetic effect) or that it may intercept a partially condensed intermediate (thermodynamic effect), the alternate orders of reagent addition were chosen on the basis that different reaction modes were operative. However, these two possibilities are not clearly distinguished by the present work since the different strategies do not necessarily dictate different mechanisms. Noting the purple color formation as soon as contact is made between $\text{EtP}(\text{VII})$ and $\text{Ni}(\text{II})$, regardless of sequencing, and assuming

There is evidence to suggest the possibility of [18-CROWN-6][1], and is tempting to suggest that all reactions involve the initial digestion of the two complex and proceed to the macrocycle via the kinetic template effect. This postulate is supported by the observation that mixtures of CROWN and NaBr do not undergo condensation even on prolonged contact. Thus, it is unlikely that the metal is receiving partially condensed material from the mixture, although admittedly the reaction could still proceed as a result of the thermodynamic effect and only have traces of the intermediate present.

The macrocyclic complex (16) was isolated in such instances as a solid by the addition of diethyl ether to the reaction mixture previously reduced to one half the original volume. This commonly used technique is based upon a lowering of the dielectric constant of a solvent mixture to precipitate ionic species from solution. However, this explanation became suspect for the present system after numerous unsuccessful recrystallizations of the complex were attempted. That is, the compounds, once isolated and dried, would not redissolve to any appreciable extent in any one of a number of solvents chosen except for DMSO in which it appeared to have limited solubility. This behavior was taken initially as an indication of some structural change taking place during the drying process because apparent solutions could be made of the "undried" complex immediately after collection on the wetted glass funnel. A further indication that structural changes might be occurring in the complex was the

Behavior in the complex could depend on the geometry,² if care was not taken to exclude atmospheric moisture from the complex during surface filtration, the complex became very sticky and darkened in color. These observations originally led the writer to the conclusion that the complex, as formed in the reaction, was composed of an octahedrally coordinated $\text{Ni}(\text{II})$ bonded by the macrocyclic ligand in the four equatorial positions and a molecule of water or solvent in each of the axial positions. Thus, this large complex ion, together with two Cl^- ions, would comprise the original solid sample collected. Upon drying, however, the additional water or solvent molecules would be removed to be replaced by chloride ions producing a neutral, insoluble complex. Thus, as long as the chloride ions were not included in the first coordination sphere, the complex would remain soluble. But this was not a particularly appealing explanation in view of one additional observation. Namely, solid material could not be collected by filtration of a reaction mixture that had been standing for several weeks. It would seem that if the complex containing chloride ions in the first coordination sphere was more stable, some of this product should have been formed during this time unless the rate of substitution was extremely slow. If one assumes that the dissolved complex (with water or solvent in the axial positions) is actually more stable, then extremely slow kinetics of displacement of the axial complex must be invoked to explain that the solid in contact with refluxing ethanol for over a week fails to produce a

solution. Because none of these explanations was satisfactory, further investigations of the system were initiated. It appeared that the solubility of the isolated, dried complex was approximately 10^{-3} M and, in fact, ultraviolet-visible spectra of these "solutions" were taken (vide infra). It was possible that these solutions could not be made more concentrated, however. Whenever a more concentrated preparation was attempted, the resulting dark brown mixture became nearly colorless upon filtering through a fine sintered glass filter and a brown solid was collected on the filter bed. The filtrate appeared to be very similar to the dilute solutions used to obtain the ultraviolet-visible spectra. This apparent incongruity was resolved when it was discovered that all "solutions", except that of CHCl_3 , exhibited the Tyndall effect. Testing of all mixtures was performed by a small laser scattering at 6328\AA . Even the original reaction mixture when diluted 10^3 proved to be colloidal, contrary to initial conclusions. A sample of the isolated solid was stirred in ethanol for 3 months and found to remain colloidal in nature. The original reaction mixture and the very dilute "solutions" of the complex appeared to behave as normal solutions and this revelation was quite unexpected because no observable solid had been collected by filtration or centrifugation of the original reaction mixture. This behavior is in contrast to solutions prepared from some dried compound and to the behavior of the reaction mixture after ether addition. In retrospect, it is fortuitous that the method of collection used in these experiments was

was transparent. The solvent system and washing techniques employed allows any impurities present to be removed from the insoluble complex along with a polar and nonpolar solvent are used. Although the complex had some solubility in DMF, the solubility was not sufficient to allow recrystallization; thus, the product was examined as isolated without further purification. In fact, the solubility of the complex in DMF was so slight that p.m.r., conductance and molecular weight data were difficult or impossible to obtain.

Characterization of the solid presented potential problems because of the possibility of contamination inherent in the collection procedures as limited by the insolubility of the product. This problem did, in fact, appear during one series of attempts to repeat the preparation. Elemental analysis of the reaction product indicated that certain organic material was included in the complex, possibly solvent or some combination of solvent and water. The product was normally dried in vacuo at ambient temperature for twelve hours to remove any volatile material. However, for some reason which still remains unanswered, one intermediate series of preparations yielded a product in which routine treatment did not remove all absorbed material. This problem was eliminated by drying in vacuo over P_2O_5 for twelve hours at a temperature of $70^\circ C$, a treatment adopted for drying the analog to this complex (vide infra).

The infrared spectrum of the [Bis(hydroxotomatoxide)] contained a recurrent absorption at 1918 cm^{-1} , which characteristically

is assigned to H_2O or $\text{H}_2\text{O} \cdot \text{HCl}$. Incorporation of adsorbed water was assigned as the source of this band as a result of the following considerations. The dried complex has a tendency to absorb water as evidenced by an observable, gradual increase in weight of the solid when exposed to the atmosphere. A qualitative test to determine the stoichiometric uptake of water per molecule of complex showed that approximately 1 molecule of water was incorporated on standing. This additional weight could be removed by vacuum drying and the process was reversible several times. The intensity of the absorption band could be reduced by preparing a KBr pellet in a plastic glove bag under a dry nitrogen atmosphere. However, the band could only be eliminated by drying both the KBr and the $[\text{Pd}(\text{acac})_2\text{Ni}(\text{Cl})_2]$ in vacuo at 75°C with subsequent loading of the KBr press in a glove bag. Scott¹² had noted that an absorption at 3343 cm^{-1} contained in the spectra of the polymeric macrocycle DTC (DTC) was assignable as H_2O . This absorption was later identified as arising from an $\text{O}=\text{C}-\text{OH}$ tautomerization which produced a $\text{C}=\text{O}$ group. The ligand in $[\text{Pd}(\text{acac})_2\text{Ni}(\text{Cl})_2]$ has the potential for this type of tautomerization, but Scott¹² had noted that the ligand reverts to the $\text{O}=\text{C}-\text{OH}$ form upon condensation. The analog $[\text{Pd}(\text{acac})_2\text{Ni}(\text{Cl})_2]$ (9b) exhibits the absorption in the 3343 cm^{-1} region also; however, it is not structurally capable of the rearrangement suggested by Scott.¹² The drying technique gave an elemental analysis which corresponded to the complex without water. The E.S.R. data were obtained from

Belleville Lake²¹ and they were instructed to dry the sample in vacuo at 75°C before analysis. The nickel analyses were performed in that laboratory following essentially the method of Flannigan.²² In these analyses, the sample was dried as above and then a volume previously determined to be the approximate amount needed for the nickel determination was quickly weighed. This sample, of course, picked up weight through absorption of water before the sample was digested in the nitric-perchloric acid mixture, but the initial weight was used to calculate the percentage composition of the metal since this weight would correspond to the free (Mr. [unintelligible]). Therefore, based on the correct analysis obtained for the carefully dried sample, the ability to remove the absorption by careful drying and the fact that no evidence could be found for a rearrangement to produce the secondary amine group in the complexed state, this absorption was assigned to the O-H stretch of incorporated water molecules. Other investigators^{21,23} have noted the inclusion of water molecules in some related synthetic macrocyclic systems. However, subjecting some of these complexes to vacuum at 100°C for 24 hours did not remove the water and in others the water could be readsorbed readily after removal. According to an X-ray study of $\text{Ni}(\text{TMAM})\cdot\text{H}_2\text{O}$ (TMV),²⁴ the water is actually occupying one of the axial coordination positions with an iodide ion positioned in the opposite site which would explain the difficulty in removing the water molecule from the complex. However, because of the

adsorption of H_2 which water could be removed from $[\text{Ni}(\text{acac})_2 \cdot \text{benzene}](\text{ClO}_4)_2$, it was concluded that the adsorption was caused by a surface phenomenon or perhaps inclusion in the lattice network and not by incorporation into the first coordination sphere of the metal.

Following the approach of Nakamoto,¹⁴ the infrared spectrum of $[\text{Ni}(\text{acac})_2 \cdot \text{benzene}](\text{ClO}_4)_2$ might be expected to be a composite of the spectra of $\text{Ni}(\text{acac})_2$ (VIII) and DAP (VIII) or might even be a composite of the spectra of $[\text{Ni}(\text{Ni}(\text{acac})_2)]$ (XII) plus DAP (VIII), except for the absence of absorptions due to the primary amine and the methoxy groups and the presence of absorption by the imine functions in the condensed rings. The amine bands would have appeared at 1660 cm^{-1} ,¹⁵ the $\text{C}=\text{N}$ absorptions as conjugated systems interact to a large extent with other double bonds in the compound and thus, it is frequently difficult to assign a definite value to this group. Bush,¹⁶ however, has reported the imine absorption of a related macrocyclic system to occur at 1570 cm^{-1} . Other studies¹⁷ have reported complicated imine absorptions between 1410 and 1435 cm^{-1} . The presence of bands in the 1600 cm^{-1} region arising from the $\text{C}=\text{C}$ grouping, the benzene ring and the pyridine ring absorptions make absolute assignment of bands in this region difficult. However, a band at 1570 cm^{-1} , not present in $[\text{Ni}(\text{Ni}(\text{acac})_2)]$ (XII) is present at moderate intensity in the spectrum of the macrocyclic complex (XI) and is assigned to the imine stretching vibration from the groups formed upon condensation. A band at 1570 cm^{-1} has been as-

the spectrum of DPF (VII) by Szwarc¹⁴ has shown that this band, arising from the pyridine ring stretching vibrations is shifted to 1405 cm^{-1} upon coordination to NiCl₂. Only these regions of the infrared spectrum were examined carefully since they would be most beneficial in structure determination. No attempt was made to assign the remaining bands although the entire spectrum is included for reference (Fig. 11).

A study of the ultraviolet-visible absorption spectrum was undertaken to ascertain the coordination geometry present in the complex (VI). As mentioned previously, solubility of the complex limited the choice of solvents to DMF and thus the concentrations possible were very low. However, the very high extinction coefficients of the complex permitted a characterization under the very dilute conditions dictated. The ϵ_{max} and extinction coefficients are listed in Table 1. DMF solutions of the complex (VI) showed a λ_{max} at 190m and a shoulder at $\sim 240\text{m}$ with extinction coefficients of 3.5×10^4 and 5.5×10^3 respectively. It was noted that the spectrum of the complex changed upon standing in DMF. Although, the change was not observable after one day, it was almost complete within one week; no additional change occurred for a period of up to 3 months. The peaks apparent in the solution on standing appeared at 202, 210, 430, 530 and 610m with extinction coefficients of the same order of magnitude as the initial solution. The spectra of ligand solutions of (VI) and the analog (VII) were noticeably different, whereas they were almost identical after standing in DMF for a period

Table 1. Ring-opening/closure polymers with [9] (9-fluorenonecarboxylic) and [10] (anthracene-9-carboxylic) in a melt phase and in various solvents.

Compound	Type of Phase and Solution (Fresh)		
	λ_{\max}	sh λ_{\max}	
9I (anthracene-9-CO ₂ H) (11)	λ_{\max} 548 $\epsilon = 7.8 \times 10^3$	sh λ_{\max} 498	
10I (anthracene-9-CO ₂ H) (12)	λ_{\max} 545 $\epsilon = 7.8 \times 10^3$	sh λ_{\max} 498	
	CHCl ₃ Solution (3 weeks old)		
9*	415	570	410 440 480
10*	λ_{\max} 420, 575, 545, 495, 460		
	Melt		
9	λ_{\max} 545 (410, 430)	sh λ_{\max} 390	
10	sh λ_{\max} 545	λ_{\max} 575	λ_{\max} 390
	Ethanol Solution (Identical after 3 days from mixture identical also)		
9**		520	470 330
10**		510	540 480 340

* $\epsilon \times 10^3$

** $\epsilon \times 10^3 = 10^3$ on these "polymers"

^{13}C -NMR spectra of 1,4-diacetylstyrene
 (a) 1,4-diacetylstyrene (b) 1,4-diacetylstyrene
 (c) 1,4-diacetylstyrene (d) 1,4-diacetylstyrene

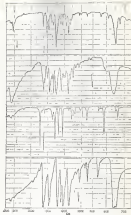


Figure 1

Table 1. Data

of one way. An attempt was made to identify the rearrangement products but a spectrum of (III) and RAP (VII) in cyclohexane (c- 10^{-4} M) was run to see if a decomposition product of RAP might be responsible for some of the absorptions. This spectrum showed no apparent absorptions in the visible region. The result is not surprising since one would not expect to see d-d transitions at these concentrations when studied in 1.0 cm cells. That fact dictates that the coordination geometry cannot be inferred from the available data on the complex, since the high extinction coefficients of the ligand charge transfer absorptions were much greater than the d-d transitions are observed.

A reflectance spectrum was taken of the complex using the mjrl cell technique. This showed a slightly different absorption pattern with the λ_{max} appearing at 575m and a shoulder at 475m. It is interesting to note that the spectrum of an ethanol "solution" of the complex was identical to that observed using the reflectance technique, except that the peaks were much more pronounced in the "solution" spectrum. A spectrum of a sample of the reaction mixture taken immediately before isolation of the complex produced identical results to those of the reflectance spectrum and the "solution" made from a dried, isolated sample. These results are consistent with the observation that the reaction mixture and the "solutions" are actually colloidal suspensions and thus should contain the complex in a form similar to the cell, i.e., the complex is merely being suspended in the path of radiation

by ethanol rather than water. The differences between the DMSO spectrum and the ethanol or water spectra indicate a change in the species present, possibly resulting from a change in the first coordination sphere of the Ni(II) . This could possibly come from the replacement of a chloride ion(s) by DMSO in the axial position(s) and would be consistent with the strong solvating properties of the DMSO. This explanation is in agreement with the data from the resonance studies (*vide infra*).

Additional evidence for axial ligation of the axial positions arises from the infrared spectrum of the product obtained from an attempt to prepare $[\text{Ni}(\text{acac})_2\text{Ni}(\text{ClO}_4)_2]$. Although this product did not give an elemental analysis corresponding to the pure product, the analyses were close and, in addition, the infrared spectrum was very similar to the $[\text{Ni}(\text{acac})_2\text{Ni}]_2$ strongly suggesting that the majority of it was the desired product. An obvious difference in the two spectra was observed in the 1150 cm^{-1} region where the perchlorate anion absorbs. The absorption for the isolated anion was markedly split, an indication of coordinated perchlorate ion. This is strongly supportive of the perchlorate occupying the axial positions and it seems reasonable that a stronger donor anion such as chloride would also occupy the set of plane coordination sites in analogous complexes.

The magnetic moment, μ_{eff} , of the complex was found to be 1.18 B.M. at 25°C and independent of temperature. This value is surprising in view of those usually reported for

$\text{Ni}(\text{II})$ complexes of either tetrahedral or octahedral geometry which fall in the range 1.45-1.55 B.M., consistent with two unpaired electrons. The high end of the range is encountered in tetrahedral $\text{Ni}(\text{II})$ complexes because incomplete quenching of the orbital angular momentum can add to the spin-only value in some complexes. The normal value observed for a low-spin, square planar coordination would be near zero, consistent with no unpaired electrons. The abnormal value determined for this complex may arise from one of two different phenomena. These possibilities will be examined after a discussion of the temperature dependence of paramagnetism, a study which seemed to offer a method of resolving which effect was operative in this particular system.

The magnetic susceptibility, χ'_M , obeys the Curie law $\chi'_M = C/T$ when idealized behavior is followed, where C is the Curie constant and T is the absolute temperature.¹¹ If this expression is strictly obeyed, $\chi'_M = 2.83 \times 10^{-5} (C)^{-1} \text{ B.M.}$ It turns out that only a few paramagnetic substances follow the Curie law while the vast majority are best described by the refined Curie-Weiss law, $\chi'_M = C/(T + \theta)$. There is no particular theoretical significance to be attached to θ except as an empirical measure of the amount of deviation from the idealized behavior expressed by the Curie law. A large value of θ ($> 25^\circ$) may indicate ferromagnetic or anti-ferromagnetic interactions in the complex. These interactions are not usually observed in mononuclear complexes because the metal centers are effectively isolated from each other by ligands so that interactions between them are insignificant, i.e.

they are ferromagnetic (10). Accordingly, a temperature dependence study of this complex was undertaken. The data presented in Table 2 and graphically in Figure 2 shows that the complex (7a) does follow the Curie-Weiss description and that the value of θ is $+8^\circ$, i.e., it is magnetically normal. The temperature studies were run down to -100°K in this laboratory using the apparatus described in the experimental section. Additional data to -4°K was graciously provided by Al Schneider in Harry Gray's laboratory at Caltech.¹¹ The two sets of independent data agree in the region of overlapping measurements and the χ_{eff} was reasonably independent of temperature over the entire range from -4°K to -100°K . A check on the reversibility of the measurements was made to determine if irreversible structural changes in the complex had occurred during the temperature variations. The results showed the magnetic susceptibility values at room temperature to be identical before, during and after the temperature dependence study, thus demonstrating that no permanent magnetically significant structural modifications had occurred as a result of the temperature variations.

The presence of the slight curvature in the plot of $1/\chi'_{\text{eff}}$ vs T prompted a closer look at the data in an attempt to determine its significance. There appeared to be three possible explanations for the deviation from the rigorous linearity expected. First, it is possible that the temperatures of the solid within the Gouy tube had not reached the temperature indicated by the external thermometer. Were the temperature

of the solid solution (from the same source indicated, the value of χ'_M would be larger and thus L/χ'_M would be a smaller number accounting for the curvature. This situation did not seem to be likely since the apparatus had been successfully used immediately before and after this experiment and the equilibration times were comparable, approximately one hour for a 10° rise in temperature. This was also the length of equilibration used by other workers on the same apparatus. It did not seem reasonable that this particular test would be plagued with extremely slow equilibration times.

Another possibility was that the sample might be undergoing a temporary phase change incorporating a different crystal form or coordination geometry dependent on temperature. Extensive study would be required to test this possibility and time limitations precluded its being undertaken. It does appear to be an unlikely occurrence although it cannot be totally excluded.

Although the deviation from linearity did fall within experimental error, it was not random. Therefore, it is highly probable that it is a fortuitous scattering of experimental points. That the data were definitely linear at the lower temperatures (as determined by a different operator on different equipment) and that the data were linear at the higher temperatures studied demonstrated Curie-Weiss behavior in those regions. Thus, it was concluded that the data were exemplary of normal Curie-Weiss behavior, especially in view of the θ values approximating zero. However, it is not to be

complex, resulting in an inconsistent derivation and the answer is left open for subsequent studies at a later date which may prove or disprove the author's conclusions.

Although the complex (3a) may exhibit $\chi(T)$ behavior that is Curie-Weiss, the magnetic moment must be considered to be anisotropic, nevertheless. The available literature contains explanations which might be invoked to account for the observed value. One general explanation has been discussed and reviewed by Nelson and Hatch,¹⁴ viz the existence of a singlet-triplet equilibrium. A series of ligands having different field strengths cause low-spin compounds with weak field ligands and high-spin compounds with strong field ligands. Consequently, the magnetic moments of complexes are expected to lie in the region of the two extremes and, indeed, this is observed in the majority of cases. It could be expected that certain combinations of ligands might provide a fortuitous example in which the energy of the high-spin and low-spin species at a given temperature would be very nearly equal. The population of the two states would then satisfy an equilibrium that is temperature dependent giving rise to a magnetic moment falling between the two extreme spin states. An equation¹⁵ has been developed to describe the behavior of χ''_M in these cases and shows that the magnetic susceptibility will decrease with temperature, opposite to the behavior predicted by the Curie-Weiss expression. Burnfield et al.¹⁶ point out that if the difference in energy between the two spin states is small, the correlation between increasing χ''_M

Table 2. Temperature dependence of magnetic susceptibility and density for $\text{Dichlorodimethylsilane}$.

$T^{\circ}\text{K}$	$\chi^{\circ}\text{M}$ (in 10^{-5}) **	$\rho_{\text{eff}}^{\text{***}}$
272.2	4.88	1.11
281.8	4.88	1.11
315.1	4.84	1.11
298.0	5.00	1.12
294.0	5.00	1.12
279.7	4.62	1.12
248.1	7.68	1.13
228.0	8.08	1.27
190.4	10.1	1.25
183.1	10.2	1.27
159.9	14.0	1.28
148.3	15.3	1.31
87.1	21.0	1.19
79.8	22.5	1.18
62.4	30.3	1.14
59.1	38.0	1.04
16.0	55.5	1.03
12.0	105.3	1.10
6.85	204.3	1.19
4.88	351.5	1.11

*Measurements taken at a temperature less than 140°K were performed at Giletech.¹⁰

**Reflects a diamagnetic correction of 129.8×10^{-6} a.g.u. units.

*** $\rho_{\text{eff}} = 1.04 \sqrt{\chi^{\circ}\text{M}^2 T}$.



Figure 2. Temperature dependence of apparent viscosity and storage modulus for P(VAc-co-MA-co-Bz).

and T does not hold in the spinel-like cases either. Nelson and Burch¹¹ have reported the preparation of a series of complexes containing a fixed quadridentate ligand coordinated in the plane of the complex with varied axial ligands in which the phenomenon just discussed was observed. The ν_{eff} of the complexes involved in the transition from high-spin to low-spin exhibited the expected temperature dependence of increasing χ''_M with T. It was therefore tempting to assume that this phenomenon was operative in the complex (9a) $[\text{Ni}(\text{acac})_2\text{mer}(\text{O}_2)]$, especially in view of the similarity of structure in the complexes. However, this explanation is not adequate in view of the results of the temperature dependence data collected which indicate normal Curie-Weiss behavior for the complex.

The other rationalization for anomalous magnetic moments involves nonequivalent $\text{Ni}(\text{II})$ ions in the unit cell, some being diamagnetic and others being paramagnetic. Several cases¹²⁻¹⁴ have been cited where $\text{Ni}(\text{II})$ complexes have exhibited this behavior. It is entirely possible that some type of mixture of square planar and octahedral species exists in the complex as prepared (the possibility of tetrahedral coordination is ruled out since the ratio of metal to donor-spacer is one to one and the only likely mode of coordination for the argonate ligand is planar). If a mixture exists, the value of ν_{eff} for this complex requires a ratio of 3:1 for low spin centers to high spin centers. The product does not appear to be crystalline (as viewed at 200X magnification)

and recrystallization could not be observed. A more satisfactory method was needed for the possibility for X-ray determination of structure to clarify the question.

Because neither explanation for the anomalous ν_{eff} was completely satisfactory, other efforts were made to resolve the problem. Attempts were made to generate the $[\text{Ni}(\text{acacetonacac})_2]^{2+}$ species with other anions in order to study the magnetic moments of the complex resulting from an axial perturbation by the anions. One might expect to see the ν_{eff} vary from essentially zero for the weak field anions to $\sim 3,2$ for the strong field anions. However, no product obtained by the template method was isolated for which a satisfactory elemental analysis resulted. The material collected in these trials undoubtedly contained much of the desired macrocyclic complex as evidenced by the similarity in the infrared spectra between the $[\text{Ni}(\text{acacetonacac})_2(\text{Cl}_2)]$ and the supposed $[\text{Ni}(\text{acacetonacac})_2(\text{X}_2)]$ where $\text{X} = \text{NO}_3^-$, SCN^- , ClO_4^- , CH_3CO_2^- , or Br^- . The solubility of the products isolated in these experiments seemed to be even less than that of the chloride complex making recrystallizations impossible. The results of the elemental analysis indicated that the product contained additional organic material and attempts were made to remove soluble impurities by repeated extraction and trituration with a succession of solvents. However, no analysis corresponding to the formulation $[\text{Ni}(\text{acacetonacac})_2(\text{X}_2)]$ was obtained and no other satisfactory formulation could be fit to the somewhat consistent analytical data received on

the "purified" product. Other macrocyclic complexes have been reported in which similar difficulties have been experienced in purification attempts.^{10,11,21}

Since direct synthesis of complexes containing ether anions was not successful, attempts were made to generate the free macrocyclic organic liquid which could then be mixed with different metal salts to generate complexes. The isolation of the free liquid prior to complexation has several advantages in addition to providing a synthetic route to new complexes. The organic product is usually more easily purified than the corresponding complex. Furthermore, the characterization of the organic product through the use of gas-liquid chromatography, p.m.r., mass spectrometry and infrared spectroscopy is normally less involved. In addition, the spectra obtained for the free liquid can be of assistance in the interpretation of the metal complex spectra. The material recovered from the experiments designed to yield the organic product was examined by thin layer chromatographic techniques and found to contain some unreacted starting material; no other product was noted by the solvent front. The retention spectrum of these materials indicated that dimerization had occurred as evidenced by the presence of peaks at higher values than 100 m/e. The free liquid parent peak at 100 m/e did not have sufficient intensity to enable one to conclude that the macrocycle had been formed. These results are not surprising because there are relatively few reported examples of macrocyclic liquids which have been synthesized in the

uncomplexed state.^{14,15,16} The attempts to produce the free ligand employed procedures similar to those reported in the literature, obviously without success.

Failure to obtain the ligand by direct synthesis, one additional approach to generate the free ligand was attempted by displacement of the metal center from the previously formed [nickelbisoxazone]Cl₂. Several methods were used to effect this goal. Addition of an ethanolic solution of sodium or potassium cyanide to a suspension of [Ni(bisoxazone)Cl₂] (9a) in ethanol led to a coarsening of the suspension, but no apparent reaction. This mixture was allowed to stand at room temperature for several hours before collecting the solid complex. The infrared spectrum of the complexed material was nearly identical to that of the original complex except for the addition of a weak cyanide absorption, presumably due to contamination. Furthermore, the percent composition of nickel was nearly the same as in the original complex. The method of Love and Powell¹⁷ was also tried. Finely ground [nickelbisoxazone]Cl₂ and potassium cyanide were stirred together in methanol for one hour. An equal volume of ethyl ether was then added to precipitate KCl and K₂O KCl, while leaving the free organic ligand in solution. However, a substantial amount of the original complex was forced down with the other inorganic salts and wash-up of the filtrate yielded no organic product. A third attempt utilized the generation of hydrogen sulfide gas by the action of concentrated sulfuric acid on solid ferrous sulfide. The gas was

passed into an ammoniacal suspension of the complex in an ethanol-ether mixture at room temperature. The gas was bubbled through for ~1 hour and the resulting solution allowed to stand for several hours. Again, a solid separated which contained unreacted complex; the filtrate was void of free ligand. These results were not unlike those found by other workers^{11,12} and demonstrate the tenacity with which the macrocyclic ligand is held by the metal. However, it may be that the extreme insolubility of the complex does not allow a mechanism for substitution alone it remains essentially in the solid state during these attempts. It is unlikely that longer reaction times would have produced different results. Lack of a substitution path may, in fact, be the cause of these observations, especially in view of the accidentally noted changes that took place in the ultraviolet visible spectrum when a DMSO solution of the macrocycle is allowed to stand for a long period (vide supra).

The very slight solubility of the complex caused a great deal of difficulty in obtaining a value for the apparent molecular weight by vapor phase osmometry. Dimethylsulfoxide was the solvent in which the complex showed the greatest solubility. In fact it was the only solvent in which any more than an extremely small amount could be dissolved. This solvent does have some inherent problems associated with its use in a vapor phase osmometer, however. This author met with repeated failures when trying to use DMSO as the solvent because equilibration times were very long and irregular

despite the fact that the L-2000-1 unit was used worked satisfactorily with other solvents such as acetone and methanol. Published research in the area using this particular solvent is unavailable. However, Dr. Bill Buck of DuPont-Bachard, Inc. manufacturer of the instrument used CHCl₃ as a solvent system with success in one instance. Correspondence with him about the problem encountered in this investigation yielded no suggestions to initiate proper response with the available instrument. Subsequently, his generous offer to attempt the analysis in his laboratory was accepted, and he was most kindly prepared [Ni(dacetonacac)(Cl)₂] (78) and [Ni(dacac)₂dmf] (79). A value of 54 was obtained for the molecular weight of the [Ni(dacetonacac)(Cl)₂] and is low, even allowing for complete ionization which will subsequently be shown to be inconsistent with conductance studies (vide infra). The calculated molecular weight for the undissociated species would be 455.8 g/mole whereas the apparent molecular weight reported if the complex dissociated into a Ni²⁺ and two Cl⁻ ions would be 184.3 g/mole. The compounds as sent were not airtightily dried as a possible time delay of one month had been indicated before the analysis could be run. Thus, instructions were supplied as how to properly dry the complexes before analysis. However, the drying procedures were neglected and the samples were run as received. As previously stated, the water incorporated into the solid does not enter the inner coordination sphere of the Ni²⁺(Cl)₂. Therefore, it is probable that the molecules of water contained in the

could simply ended up in solution as discrete particles. The additional entities created or dissolution would certainly lower the apparent molecular weight of the species. However, the value of 58 obtained by experiment would require not only complete dissolution of the macrocycle but, in addition, approximately seven molecules of water per complex that dissolves, a highly unlikely situation. The point that is noteworthy is that the low rather than a high value indicates the nature of the complex is not a colloidal suspension, consistent with the laser studies of the DMG solutions which also disproved the existence of colloidal particles.

Characterization of the compound by conductance studies proved to be difficult also, again because of its limited solubility in all solvents but DMG. The conductance study was undertaken to elucidate the composition of the complex in terms of whether monomeric ionic entities were dissolving or whether it was some type of oligomer. The possibility of having the chlorine atoms bonded to the organic moiety was entertained as an explanation of the solubility characteristics. The molecular weight data must doubt as any form-

lation is solvation except the ionic case but the ambiguity of these results prompted further investigation to answer these questions.

The DMF system has been studied as the solvent for various electrolytes and is reviewed by Geary²¹ with respect to its use as a solvent for coordination compound characterization through conductance studies. Allen et al.,²² and Ramey-Regnier et al.,²³ have studied complexes of 2:1 electrolytes in DMF and the latter have found the molar conductance, Λ_m , to be $28 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ for the complex $[\text{Ni}(\text{en})_2(\text{O}_2\text{CCH}_2)_2]$ $[\text{Et}_4\text{N}][\text{BF}_4]_{1.1}$. This value was obtained at 25°C and 10^{-3} M concentration and is consistent with a formulation of a 2:1 electrolyte according to the authors. The conductance data collected on the $[\text{Ni}(\text{acac})_2\text{en}][\text{Cl}]$ and the $[\text{Ni}(\text{acac})_2\text{en}][\text{BF}_4]$ is listed in Table 3, and shown graphically in Figure 3 and seems to be consistent with a degree of dissociation which is somewhat less than complete.

The fundamental objective of this conductance study was to determine the extent to which the complex dissociated in DMF solution. A side effect to be considered involves the influence of traces of water in the conductance of DMF. This effect would be of concern when using DMF because of the hygroscopic nature. In fact, Butler²⁴ points out that none of the methods used to purify DMF was effective in removing all of the water. Vigorous percolation in removing water did raise the resistance of the solvent; but, simple drying at DMF over molecular sieves had little effect on the conduct-

Table 1 Conductance of $\text{Et}(\text{acetoxymer})\text{Cl}_2$ at 25-35°C.A) For dissociation Path $\text{EtX}_2 + \text{Et}^{\text{Et}} + 2\text{X}^-$

Solution	$\Sigma \kappa \cdot 10^4$	$\Sigma \kappa \cdot 10^4$	Λ	$\Lambda^{\text{Et}} \cdot 10^4$
DMF	1.529	"	"	"
1	4.14	3.886	32.39	1.388
2	8.43	4.431	33.14	2.110
3	14.50	8.268	19.98	2.879
4	23.80	12.77	18.49	3.354
5	31.89	17.94	17.03	4.239
6	42.22	25.41	16.63	5.061

B) For dissociation Path $\text{EtX}_2 + \text{EtX} + \text{X}^-$

DMF	1.516	"	"	"
1	4.14	3.813	44.89	1.9819
2	8.41	3.325	42.29	1.492
3	14.50	4.133	39.83	2.033
4	23.80	6.388	37.31	2.527
5	31.89	8.999	35.84	2.977
6	42.22	12.71	33.23	3.845

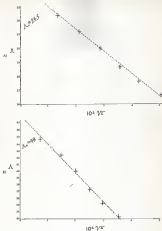


Figure 3. Temperature dependence of activation energy for polyisobutylene ($10^4/T$).

- (a) Linear data used in correlation model $\ln A_0 = \ln A_0^0 - 1/T$
 (b) Linear data used in correlation model $\ln A_0 = \ln A_0^0 - 1/T$

used. A determination of the conductance of freshly opened Fisher Reagent Grade DMSO gave a conductance value in agreement with that previously reported. Further tests were conducted in this laboratory to ascertain the effect of additional water on the conductance. The results indicated that addition of up to two percent water does not increase the conductance. Thus, it was concluded that the water contained in the DMSO does not contribute significantly to the conductance at these levels. The other concern was whether the water would have an effect on the displacement of the chloride ions in the first coordination sphere of the macrocyclic complex. This effect was considered negligible since since the complex exhibits essentially no solubility in water and it seems unlikely that the presence of water would enhance the displacement of the chloride ions to produce a greater number of separate ions in solution. Therefore, confidence was established that the effect of water would not be significant on the values determined for the conductance, and the discovery of other experimental results reported where DMSO was used directly from the supplier led this author to follow that practice in this work.

The Onsager equation,¹⁷ $\Lambda = \Lambda_0 - S\sqrt{C}$, provides a description of the behavior of electrolytes in solution, where Λ = equivalent conductance, Λ_0 = limiting equivalent conductance and C is concentration with S being a constant relating Λ and \sqrt{C} . If Λ decreases with an increase in concentration, the system is behaving as an electrolyte.¹⁸ Plots for the system

[Data from Figure 1] given in Figure 1 show this relationship between γ and C . Furthermore, the plot of λ versus \sqrt{C} (Fig. 1) is a straight line as would be expected from the Debye-Huckel equation.

These data support ionic dissociation of the compound in DMF solution. If the solute is a well behaved electrolyte, an additional equation, $\lambda = \lambda_0 + B$,²² can be used as a check against experimental data. Here, B and λ_0 are the same terms found in the Debye-Huckel equation while λ and B are constants for a specific ion and solvent and values for λ and B have been calculated.²² The plot of λ versus \sqrt{C} is obtained from experimental data with the intercept yielding λ_0 and the slope yielding B . The theoretical slopes obtained from the equation above can be compared with the experimental slope from the graph. If the experimental and calculated slopes are different, it can either mean that the type of dissociation postulated is not being followed or that the complex is this type of electrolyte but is remaining associated. Most data have been collected on the 1:1 electrolyte systems but data to one source²³ does calculate λ and B for 2:2 electrolytes; thus, a comparison of the theoretical and experimental slopes for this system is possible based on both a 1:1 and a 2:2 electrolytic behavior, i.e., $\lambda_{2:2} = \lambda_{1:1}^2 + 2$ or $\lambda_{2:2} = 2\lambda_{1:1}^2 + 2$ dissociation paths. The results of these calculations are shown in Table I. They indicate that the dissociation behavior is not that of either ideal case but is probably somewhere in between the two.

The same conclusion can be drawn when the contribution of each specific ion to Λ_0 is taken separately. The value of Λ_0 should be approximately a sum of the individual ions. Chloride ion in DMSO has a value of Λ_0 equal to 21.0.²¹ Another source²² notes that large positive ions have Λ_0 values less than 25.0; a value of 18.5 has been reported for Me_4N^+ , where Me = methyl and N = N carbon atom chain. Using these values and calculating Λ_0 for the $\text{Me}_4\text{N}^+ + \text{Me}_2\text{S}^{2-} + \text{X}^+$ type of dissociation, Λ_0 would fall somewhere between 24 and 28. The observed Λ_0 assuming this type of dissociation was 28 which would require such too high a value of Λ_0 for Me_2S^{2-} . For the $\text{Me}_4\text{N}^+ + \text{Me}_2\text{S}^{2-} + 2\text{X}^+$, Λ_0 would fall between 21 and 26, again assuming a value of ten or less for the positive ion. The observed value was 28 when the data were graphed assuming this pathway and is much too low, not even accounting for the two chloride ions' contribution to Λ_0 . Since 5 has a concentration ten in the denominator for the ions, the actual situation seems to be one in between the two ideal cases of dissociation.

One arrives at the same conclusion by calculating the value of the specific conductance, κ , at a given concentration. However, the procedure is very similar to the method of comparing the theoretical and observed Λ_0 . Again the results did not conform to either ideal path of dissociation but rather to a situation in between the two. Therefore, the complex [5a] tends to behave as an electrolyte in the DMSO solvent but it does not conform to an ideal case of dissociation.

Two additional qualitative tests were used to characterize the macrocycle $[\text{Ni}(\text{trichloromethyl})\text{Cl}_2]$. The first of these studies was in DMF solution and involved the precipitation of Ions as insoluble chloride as silver chloride to determine the species present in this solution. The first attempts to precipitate the chloride ion with silver ion in DMF were unsuccessful, because the solution of the silver species complex itself is so highly colored that it masks the visual appearance of the silver chloride. Silver nitrate was added in ten percent excess based on the availability of two moles of chloride ions per mole of complex. Another difficulty encountered was that the silver chloride did not appear to form a precipitate immediately at the concentrations of 10^{-3}M in macrocycle and 10^{-1}M in silver nitrate which were used. Part of this observation may have been simply due to the intense color of the species which masked the AgCl particles. The particle size of the precipitate produced was too small to allow collection by filtration and "digestion" did not be used to increase particle size because the increased temperature decomposes the silver chloride in DMF.¹² To circumvent the inability to collect by filtration, the species was centrifuged for an hour at moderate speed and the excess DMF decanted. This procedure allowed recovery of approximately forty per cent of the theoretical amount of chloride based on two insoluble chlorides per molecule and was considered sufficient to demonstrate that the complex contained ionic or potentially removable

chloride ion. Consequently, the tedious procedures of Lashro *et al.*,²² were not employed to ensure the recovery of all the silver chloride precipitate to allow for analysis of the chloride.

The second series of qualitative tests were employed to show the stability of the $[\text{Ni}(\text{acac})_2(\text{Cl})_2]$ complex when exposed to acid treatment, as resistance to acid hydrolysis was one of the features common to analogous neocuproline complexes. In order to determine the stability, a suspension of the solid complex in concentrated hydrochloric acid was kept at 45°C for a period of one hour at reduced pressure while the acid was being removed on a rotary evaporator. The solid remaining was analyzed for percent composition of nickel and found to be well within the expected range for $[\text{Ni}(\text{acac})_2(\text{Cl})_2]$. In addition, the infrared spectrum of the acid treated sample was identical to untreated samples of the complex. Another sample was subjected to concentrated nitric acid for nearly two hours under identical conditions to the hydrochloric acid treatment. The sample showed effervescence when the first contact with the acid was made but no reaction was noted after this initial one. This reaction was presumed to be the oxidation of chloride ion to chlorine after examination of the remaining solid showed minimal loss of compound. Also, the solid remaining after the acid was removed by reduced pressure showed an identical infrared spectrum to that shown by the solid obtained from the attempts to prepare the $[\text{Ni}(\text{acac})_2(\text{Cl})_2]$ of by direct synthesis when using nickelous nitrate as the NiCl_2 ion source. Both

of these spectra are similar to that of the [Rifam-
metamtrCl₂] except for the presence of an intense nitrate N-O
absorption mode¹²⁻¹⁴ at ~ 1375 cm⁻¹. The compounds obtained
from the nitric acid treatment of the chloride complex and
the direct synthesis using the nitrate salt could not be
found to give the correct analysis for nitrate assuming a
formulation of [Rifametonate](NO₃)₂. The solubility of
these two compounds seemed to be much less than the chloride
analogue although no quantitative data was taken and thus re-
crystallization was not effected.

Several attempts were made to obtain a mass spectrum of
the compound. In each case, subjecting the sample to 300°C
in the sample port produced a spectrum with no peaks of
sufficient intensity over the back ground to account for
the molecular ion or any fragment. This observation is
equivalent with the compound being ionic and supports the
data found in the molecular weight and conductance studies.

Although the characterization of the complex [Rifam-
metamtrCl₂] (vii) does not allow a definite conclusion to
be drawn about structural features, the data collected
represents an extensive use of readily available techniques.
It does appear that the formulation of a nickel ion sur-
rounded by a hexamously bridged square planar ring with two
chloride ions occupying the axial positions of the coordina-
tion sphere is at least consistent with the data. Other
systems¹¹⁻¹³ have met with the same or more difficulty in
characterization and similar conclusions have been drawn.

8. $\text{Os}(\text{acac})_2\text{osac}(\text{Cl})$

The successful preparation of $\text{Os}(\text{acac})_2\text{osac}(\text{Cl})$ logically led to attempts to synthesize structurally related compounds. In the selection of precursors to these analogs, consideration was given to the steric strain present in $\text{Os}(\text{acac})_2\text{osac}(\text{Cl})$ as suggested by a Framework Molecular Model. Specifically, the apparent strain involved the two methyl groups on the $\text{Os}(\text{VII})$ moiety. The steric interactions between methyl groups and the benzene rings might cause a peaking of the macrocycle, which in turn would affect the distance of closest approach for the set of plane coordination sites. It was anticipated that this effect, if significant, would be reflected by the magnetic susceptibility of the compound. If the axial distances are indeed significantly altered, the coordination of the complex would vary from an octahedral, high-spin case for close approach to a square planar, low-spin case for long axial distances. Even though the observed anomalous magnetic susceptibility of the $\text{Os}(\text{acac})_2\text{osac}(\text{Cl})$ complex was inconsistent with either limiting case, it was attractive to pursue investigations of analogs to $\text{Os}(\text{acac})_2\text{osac}(\text{Cl})$ in an effort to identify the source of the unusual experimental value of the magnetic moment.

Accordingly, 2,4-pyridinedicarboxaldehyde (PDC, IX) was selected as the carbonyl containing reactant, replacing the methyl groups at $\text{Os}(\text{VII})$, a precursor of $\text{Os}(\text{acac})_2\text{osac}(\text{Cl})$, with hydrogen atoms. A Framework Molecular Model shows that this change allows the macrocycle ligand to assume a completely planar configuration without steric strain.

Thus, the monomers chosen to condense into the final mesogenic liquid were POC (IX) and OCTMAB (VII) in a one to one stoichiometric ratio. The dialdehyde compound (IX), at one time commercially available, had been shown to undergo Schiff base condensations and some of its complexes were subsequently studied.⁷⁴ Thus, it was ideal for incorporation into the mesogenic analog of [Si(phenylthiomethyl)Cl]₂. Unfortunately, the POC (IX) was no longer available because the process from which it was derived as a by-product had been discontinued.⁷⁵

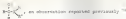
Accordingly, it was necessary to prepare the POC (IX). In principle, the compound can be synthesized by a three-step process. After preparing the methyl-ethyl ester of 3,4-pyridinedicarboxylic acid (XVI), one can convert it to the diolcohol (XVII) by reducing it with lithium aluminum hydride.⁷⁶ Subsequently, the alcohol (XVII) can be oxidized to the desired dialdehyde (POC, IX) with manganese dioxide.⁷⁷ This synthetic route was attempted, but, it met with only limited success because the reduction step resulted in extremely low yields of the diolcohol (XVII). The desired dialdehyde was successfully and straightforwardly prepared but the small amounts of the precursor alcohol (XVII) limited the quantity possible. Preparation of the dialdehyde (IX) in larger quantities was possible when the alcohol precursor became commercially available. The oxidation of the alcohol to the aldehyde group was carried out following the method of Papadopoulos, *et al.*⁷⁸ Purification of the dialdehyde (IX)

was effected by column chromatography employing a silica gel column and eluting with an eighty percent benzene-twenty percent ethyl acetate mixture. The middle fraction of eluent was found to contain the pure dialdehyde after removal of solvent. This purification procedure was adopted after the reported literature method for acetylation was found to be inadequate. Interest in obtaining the starting materials as pure as far as possible was indicated in an effort to reduce the introduction of other organic compounds into the reaction mixture. Reflection upon the properties of $[\text{Ni}(\text{acac})_2(\text{Cl})_2]$ had led to the conclusion that if the proposed analog behaved similarly, there would be no convenient way to purify the product once formed. Thus, it seemed essential to carry out the synthesis with compounds as pure as possible.

The first attempts to synthesize $[\text{Ni}(\text{acac})_2(\text{Cl})_2]$ paralleled the three methods previously found to be unsuccessful for the preparation of $[\text{Ni}(\text{acac})_2(\text{Cl})_2]$. The "analogous reaction", i.e., slow addition of the ethanolic cerous HCl solution to a refluxing ethanolic solution of the nickel $(\text{Cl})_2$ chloride salt and HCl (10) was tried first because it seemed to offer the most logical promise of success after investigating the preparative routes used for the beta analog. A red-brown solid was isolated which was characterized by an infrared spectrum very similar to that of $[\text{Ni}(\text{acac})_2(\text{Cl})_2]$. However, the elemental analysis showed a low value for nickel (12.22) and nitrogen (3.85) and a high value for the carbon (34.88) and hydrogen (3.72) relative to the values

calculated for a β -hydroxyketone (1) = 13.80, 14.49, 16.75 and 16.85 percent, respectively. The procedure was repeated several times to more carefully handle and collect the product because of the confidence placed in the potential success of this method. There was sufficient variation in the elemental analyses for the product collected in these initial experiments that no assignment of a definite formulation was attempted. Nonetheless, this author believed that the solid contained some of the desired β -hydroxyketone (1) because of the similarity in physical properties to those of the keto analog. Namely, the color changes observed during the course of the reaction were similar to those observed during the preparation of β -hydroxyketone (1) and the infrared spectra were very similar. There appeared to be two rational explanations for the inability to isolate the pure β -hydroxyketone (1). One of these explanations was that the desired product was indeed formed, but with inclusion of solvent and/or water. This rationalization was attractive in view of the analytical results but would imply that, for some reason, the material did not have the adhered solvent and/or water removed by drying *in vacuo* for 12 hours at ambient temperature, the same treatment found successful for the keto system.

The second proposed explanation concerning the inability to isolate the β -hydroxyketone (1) complex was that the carbonyl and amine functions, although participating, did not eliminate a water molecule and produced in the double-bonded Schiff base. This would produce an amine-carbinol intermediates,



The infrared spectra were not as helpful as they normally would be in defining which, if either, of the possibilities reported was correct. Specifically, this difficulty was due to the presence of a broad intense absorption at 3334 cm^{-1} . Absorptions in this region are undoubtedly due to OH and/or NH stretching modes; but, the band was so broad that it could not be sufficiently resolved to assign any specific vibrational modes. The broadness of the band was considered to result from hydrogen bonding; it is significant to note that this same band is present in the spectrum of the keto analog; at a much later point in time during the course of these investigations a method was found to remove the contaminants (solvent and water) responsible for the band (vide infra).

Continuing to operate on the assumption that some of the desired product was present in the solid collected, several different techniques of recrystallization were used in an effort to purify the product. At the time, sample attempts to recrystallize the compound from methanol or ethanol, as well as from solvent mixtures, produced rather unusual and inconsistent results. At one point a mixture being used for recrystallization was put on a sintered glass filter with no solid being retained on the filter; however, when the "filtrate" from the first filtration was passed through a fine sintered glass filter, a solid which had

method used to prepare the keto analogs. Using the pre-formed $[N]COC(=O)N-Cl$ (XII) as a starting material together with POC (IX) produced comparable results to the two methods described previously. Thus, none of the three procedures found successful for the keto analog was successfully employed for the preparation of $[N]C(=O)NOC(=O)N-Cl$ (VII).

The first, new modification in procedure involved changing the sequence of addition for the starting materials, so that there was not a large excess of either organic position. Ethanol solutions of COC(=O)N (VII) and POC (IX) were placed in separate dropping funnels and added simultaneously and slowly to a refluxing ethanol solution of nickelous chloride producing a red-brown solid; the solid was not the desired $[N]C(=O)NOC(=O)N-Cl$ but rather a product which exhibited the same characteristics noted in the prior attempts, viz., incorrect elemental analyses and an infrared spectrum similar to that of $[N]C(=O)NOC(=O)N-Cl$.

One possible explanation of the inability to obtain $[N]C(=O)NOC(=O)N-Cl$ involved the formation of the amine-carbamate from the carbonyl and amine rather than the Schiff base. Even though the elemental analyses did not conform to a specific formulation involving the amine-carbamate structure, the fact that the drying process employed up to this point did not remove the "moisture" suggested that they might be bonded and/or distributed in a different manner than was observed for the keto analog. If the amine-carbamate

process was not complete. The "curing" would not likely remove a water molecule, a feature consistent with the reported literature.⁷⁰ In an effort to enhance the equilibrium position for the completed condensation, $(\text{Et}_3\text{glyme})_2\text{Cl}_2$ was used as the source of Et_3N . Therefore, the only water in the system should come from the elimination step of the completed condensation. However, elemental analysis of the product prepared from the $(\text{Et}_3\text{glyme})_2\text{Cl}_2$ did not conform to the desired macrocyclic complex.

The next attempt to create a favorable equilibrium position for the elimination step involved the use of a dehydrating agent that would drive the reaction on to the desired Schiff base by removal of a water molecule from the hydroxy intermediate. The method of dehydrating that was tried first involved addition of 15 to 30 ml of 2,2-dimethoxypropane (VII) to the preparations which followed identically the three successful methods utilized in the $(\text{Et}_3\text{N})_2\text{SO}_4/\text{Et}_3\text{N}$. This method did not produce favorable results as the product isolated had an even lower molar content (18.4% percent) than the preparations where no dehydrating agent was added. In fact, the absorption at 1720 cm^{-1} in the infrared spectrum was assigned to an unexpected carbonyl group which, if coming from the H_2O (II) starting material, would indicate that condensation had not occurred. Another possible but unlikely source of the carbonyl absorption did exist, i.e., the 2,2-dimethoxypropane prepolymer products are methanol and acetone; but, it is difficult to rationalize the incorporation of

appreciable amounts of isomers with the product isolated. Had the isomeric molecules been trapped in the lattice network of the complex, it is unlikely that they would remain in the lattice after subverting the complex to 8 to 12 hours in vacuo.

Some of the solid product produced via the above technique was suspended in 2,2-dimethoxypropane for various lengths of time and at different temperatures in an effort to drive the condensation of the carbonyl and amine groups to completion. These modifications did not seem to alter the product in any manner. In fact, one of the samples analyzed after this type of treatment yielded a nickel composition of 3.56 percent, the lowest of any isolated solid in the experiments designed to produce $(Ni_{1.00}Co_{0.00}Al_{0.00}O_{1.00}Cl_{1.00})$.

Since simple addition of the dehydrating agent to a reaction mixture did not result in the successful isolation of the desired complex, an obvious extension of the process was to use 2,2-dimethoxypropane (DMF) as the solvent. Again, the three basic methods found successful for preparing the $(Ni_{1.00}Co_{0.00}Al_{0.00}O_{1.00}Cl_{1.00})$ were followed except for using 2,2-dimethoxypropane rather than ethanol as the solvent. These preparations also led to a product similar in physical appearance to that of $(Ni_{1.00}Co_{0.00}Al_{0.00}O_{1.00}Cl_{1.00})$ but with low nickel analysis as compared to the theoretical value for $(Ni_{1.00}Co_{0.00}Al_{0.00}O_{1.00}Cl_{1.00})$. In addition, the infrared spectrum of the solid continued to exhibit a carbonyl absorption as it did in the experiments where 2,2-dimethoxypropane was just added to the regular reaction mixtures.

The same experimental procedures were followed again but with tetrachloroethersulfonic acid (TCEA) replacing the 2,2-dimethoxypropane as a dehydrating agent. This attempt also failed to yield the pure $[\text{Ni}(\text{acac})_2(\text{Cl})_2]$ as evidenced by the low signal intensity obtained.

A suggestion to try a 4:1 by volume tetrahydrofuran/ H_2O as a solvent system resulted from consultation with Dr. J.R. Kuyup¹² about the synthetic approaches to the desired $[\text{Ni}(\text{acac})_2(\text{Cl})_2]$. This mixture was used as the solvent while the procedures patterned after the successful bipy preparations were followed but no useful product was able to be isolated from any of the attempts.

Since none of the previously described experiments resulted in the isolation of the desired macrocyclic complex (VII), a critical evaluation of the system and conditions was undertaken. It is known¹³ that the aldehyde functionality is more sensitive than the ketone, so it was questioned whether the conditions employed in the previous reactions were leading to unwanted reaction products via other reaction paths. Presumably then, less severe conditions could be used to effect the preferred condensation. Three additional parameters were selected as variables: the amount of acid catalyst, the length of reaction and the temperature. Removal of the external acid had actually been effected during some of the previous experiments, because it was suspected that the equilibrium conditions involving the formation of an imine linkage from an aldehyde starting material might be affected

to a greater degree than in the $\text{HNO}_3\text{-PbO}_2$ case. A systematic series of experiments was then conducted in which procedures paralleling the three successful routes for the beta system were carried out except that no mineral acid was added. These experiments produced solids having the same properties as those noted when additional mineral acid was used, i.e., not the desired monomeric complex. Similar observations are not surprising in the light of a later discovery, namely that a proton is lost from an amine function whenever a complex is formed with COCl_2 . Nonetheless, there should not have been any additional acid remaining after the condensation was completed since the acid generated in the formation of the of the same complex is used up stoichiometrically by the subsequent formation of the Schiff base from the amine complex.

Several experiments were next conducted using the three basic methods employed for the beta system but in which the length of reaction was varied from one to forty-eight hours. The products obtained from this series of preparations were very similar to solid, texture, spectral properties and elemental composition to those collected in prior preparations. Thus, no $[\text{Ni}(\text{acac})_2(\text{OCl})_2]$ had been isolated from any of the approaches up to this point.

A reduction in the reaction temperature represented the third attempt to reduce the severity of the conditions. It turned out that the attempts to prepare the pellets of the $[\text{Ni}(\text{acac})_2(\text{OCl})_2]$ under very dry conditions were being

condensed H_2O removed. These columns were subjected to temperatures of 70 to 80°C in vacuo over P_2O_5 in order to remove the water. Since the equipment was set up and in operation, the solid from the preparation described below was also dried in this manner. The "template reaction" was used following exactly the method used for the [Si(monoalkoxy)(Cl)] except that the temperature of the reaction system was kept at 40°C, instead of refluxing ethanol. The product prepared in this experiment and dried as described for 12 hours produced the pure [Si(monoalkoxy)(Cl)] as evidenced from elemental analysis and characterization described later. The product as isolated from the reaction and dried in vacuo at ambient temperatures for the same period of time retained what corresponds to roughly 0.5 mole of ethanol and 0.5 mole water per mole of [Si(monoalkoxy)(Cl)]. The desired complex can also be prepared by the "delay reaction" and by the method using the preformed [Si(DCCOAH-2)(Cl)] as one of the starting materials, as long as the solid isolated from the reaction vessel is dried in vacuo at the elevated temperature. The similarity of the infrared spectra of the desired product and the previously isolated products gives reason to believe that many of the other methods of attempted preparation would have produced the [Si(monoalkoxy)(Cl)] had the proper drying technique been employed. This assumption was not checked, however, because the main thrust of this research was to synthesize a suitable product, not to exhaust all possible methods of preparation.

The reaction preparation used a few drops of concentrated hydrochloric acid as a catalyst for the indole bond formation. As with the $(\text{Ni}(\text{acac})_2\text{O}(\text{Cl})_2)$, there was an systematic study undertaken to determine if the acid catalyst was necessary for the production of the heterocyclic complex. However, the stability of the complex to acid treatment was tested in a manner similar to that used for the $(\text{Ni}(\text{acac})_2\text{O}(\text{Cl})_2)$ system. Some of the solid $(\text{Ni}(\text{acac})_2\text{O}(\text{Cl})_2)$ was suspended in concentrated hydrochloric acid at a temperature of 50°C and held at this temperature for a period of one hour while the acid was removed on a rotary evaporator. The solid remaining was found to contain 13.15 percent nickel, a value equal to the theoretical value of 13.11 percent within experimental error. In addition, the infrared spectrum was identical to an untreated sample and there was minimal loss of solid, indicating no significant decomposition had occurred on exposure to concentrated acid. The remaining characteristic action of $(\text{Ni}(\text{acac})_2\text{O}(\text{Cl})_2)$ follows very closely that of the analog $(\text{Ni}(\text{acac})_2\text{O}(\text{Cl})_2)$. The experimental data and the conclusions drawn from it will be presented in the following text, although much of the background presented in Section A for the $(\text{Ni}(\text{acac})_2\text{O}(\text{Cl})_2)$ complex will not be repeated because of its redundancy.

The infrared spectrum of the $(\text{Ni}(\text{acac})_2\text{O}(\text{Cl})_2)$ is shown in Figure 4. It is very similar to the analog made from the ketone precursor. The spectra of $\text{Ni}(\text{O}(\text{C}=\text{CH})_2)_2$ (12) and 2,4-pyridinedicarboxaldehyde (13) are shown as the

precursors of the macrocyclic complex. As discussed in [Ni(aldol-ketomacrocyclic)]₂, the spectrum is seen to be nearly a composite of the precursors except for the appearance of absorptions arising from the carbonyl stretch and the coordinated primary amine NH and deprotonated amine NH stretching. The new amine amide absorption is obscured by the confusion of C-C, C-H (pyrrolidine) and N-H absorptions which were already present in the precursor molecules and absent in the same region of the spectra as the newly formed amide/amine linkages. The absorption around 3150 cm^{-1} is discussed in the [Ni(aldol-ketomacrocyclic)]₂ section.

The solubility of the complex proved to be extremely low in all solvents used, resembling that of the [Ni(aldol-ketomacrocyclic)]₂. Very high extinction coefficients allowed spectra in the ultraviolet and visible region to be taken in DMF. These data are shown in Table I. The λ_{max} and extinction coefficients are very similar to those found for the [Ni(aldol-ketomacrocyclic)]₂, reflecting the formal and actual similarity of the two complexes. [Ni(aldol-ketomacrocyclic)] exhibits the same solution phenomena as its analog, also. Namely, a true solution is obtained in DMF, whereas the ethanol mixtures are colloidal. The reaction mixture, the original salt and the prepared "solution" from isolated and dried compound are all very similar for the macrocycle and no change is noted in the ethanol "solution" for up to 3 months. In contrast to this behavior is the fact that DMF solutions change on standing as was the case with the keto analog. This effect is not noticeable after 1 day

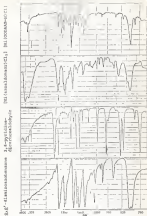


Figure 4

Infrared Data

but seems to be rather complex since it does. Comparison of the ultraviolet-visible spectra for the add and keto macrocyclic indicate some obvious differences in the absorption pattern as well as similarities. Visual appearance also indicated a slight difference in color of the two solutions. The differences become more striking when it is noted that the basic macrocyclic rings for the two complexes are identical, the only difference being a change in substituents attached to the conjugated system. This change in structure should have relatively little effect on the charge transfer species.¹⁰ It is therefore entirely reasonable to assume some other effect is operative in the two systems which causes the difference in spectra. This effect could well be the steric effects mentioned earlier which prompted the synthesis of the [Ni(dmpo)(dmsac)(Cl)]₂. The presence of the methyl groups in the keto system may cause sufficient packing to exist in the macrocyclic ligand so that the charge transfer bands are affected slightly.

The magnetic moment of [Ni(dmsac)(dmsac)(Cl)] was determined to be 3.16 ± 0.20 B.M. at various temperatures for several measurements where the temperature varied from $21.9 \pm 0.4^\circ\text{C}$. The temperature dependence data are presented in Figure 3 and Table 4. The observed magnetic moment represents an anomalous value for $\text{Ni}(\text{Cl})_2$, i.e., it corresponds neither to a normal square planar geometry ($\mu_{\text{eff}}^2 = 0$) nor to a normal octahedral geometry ($\mu_{\text{eff}}^2 = 2.8$). An anomalous value was obtained also for the keto analog and the two possible explanations for the values observed in the keto compound would apply for this complex. The

possibility is a glass-transition point involved causing the anomalous behavior reported in a temperature study of the magnetic susceptibility. This line (Figure 3 and Table I) shows a normal Curie-Weiss behavior with a value for θ being approximately zero as given by extrapolation of the $1/\chi_{eff}$ vs T plot. Thus, as for the keto case, this type of temperature dependence discounts a singlet-triplet equilibrium. The values from -4°K to -100°K were measured at Caltech¹² while the range studied in this laboratory was from -150° to -100°K . The other possible explanation for χ_{eff} values other than the normal high spin or low spin value involves a mixture of different types of coordination in the bulk solid. If this is the case for $[\text{Ti}(\text{acac})_3\text{Cl}]$, then the ratio of high spin to low spin would be 1:1. As stated previously, one of the reasons for preparing this compound resulted from a study of Frankish Molecular Models which indicated that a considerable amount of steric interference would be present in the planar ligand of $[\text{Ti}(\text{acac})_3\text{Cl}]$ as compared to the enantiomer. It was tempting to speculate that the out of plane coordination sites would become more accessible in the solid compound and thus allow an octahedral geometry to be more nearly realized. Thus, the χ_{eff} should be larger in the solid acac complex. This, in fact, was observed; but, the temperature dependence data does not support this original postulate which should show a marked dependence of χ_{eff} on $T^{\circ}\text{K}$. Therefore, the only reasonable conclusion is that the packing for the two complexes creates two different types of geometry

Table 4. Temperature dependence of magnetic susceptibility and moment for $(\text{Ph}_3\text{C}_6\text{H}_4\text{NMe}_3)\text{Cl}_2$.

$T^\circ\text{K}^\circ$	χ^*_M (in 10^{-5}) ^{***}	μ_{eff} ^{***}
343.4	1.58	2.21
343.0	1.63	2.27
363.4	1.78	2.35
$\mu_{\text{eff}}^{\text{****}}$	1.86	2.38
383.8	1.94	2.42
396.7	1.99	2.45
457.8	2.31	2.54
527.1	2.56	2.62
596.5	2.94	2.78
669.4	3.30	2.88
743.9	4.05	2.97
818.4	4.95	3.12
896.8	5.32	3.16
1000.8 ^{***}	6.55 ^{***}	3.49
81.8	6.67	3.48
90.8	6.67	3.47
81.9	13.66	3.66
12.6	17.46	3.81
21.8	26.81	3.98
51.2	42.58	4.56
4.20	78.61	5.38

*Measurements taken at a temperature less than 100°K were performed at Caltech.¹⁻³

**Reflects a diamagnetic correction of 100.8 in 10^{-5} c.g.s. unit.

*** $\mu_{\text{eff}} = 2.84 \sqrt{\chi^*_M RT}$

**** μ_{eff} values represent an average of seven measurements made on the sample over a period of 2 months (compound was kept at dry ice 7% in vacuo between measurements).



Figure 5. Temperature dependence of magnetic moment and Curie temperature for Mn^{2+} ions in MgO .

around the $\text{Mg}(\text{H})$ making some of them low-spin and some high-spin as the ratios previously tabulated. Confidence in the data results from the same considerations used in the keto analysis: 1) agreement of χ_M values taken at two different field strengths, and 2) agreement of data taken by two different investigators employing different techniques. The solution value of χ_{eff} was not obtainable by the Gouy or g.m.r. method due to the limited solubility of the $[\text{Mg}(\text{acac})_2(\text{H}_2\text{O})_2]$ and $[\text{Mg}(\text{acac})_2(\text{H}_2\text{O})_4]$.

Synthesis of the complex with different solvents was attempted in an effort to clarify the explanation for the χ_{eff} values. As was the case with the keto system, there was no success in isolating any purified complexes from these experiments.

One additional magnetic susceptibility study was conducted on the $[\text{Mg}(\text{acac})_2(\text{H}_2\text{O})_2]$ complex to further characterize the complex. As noted previously, the solid collected from the reaction mixture and dried in vacuo at ambient temperatures corresponded roughly to the desired complex with 0.5 mole ethanol and 0.5 mole water per mole of complex. It would be of interest to know the nature of these solvent molecules in terms of whether or not they were included in the first coordination sphere of the metal. Were they indeed located in the immediate vicinity of the metal center, the removal of these and the presumed replacement of them with the chloride ions should have an effect on the observed magnetic moment. A temperature dependence determination was

conductance on a sample whose resistance the solvent; it was found to obey the Debye-Hückel law and to possess a κ_{cell} identical to that of the subsequently dried sample. This demonstrates that the solvent was incorporated into the complex in a manner other than in the first coordination sphere of the metal. The rather consistent amount of solvent inclusion in the sample suggests that it might occupy specific lattice sites. Therefore, these observations, coupled with the absence of any complexes of Sn(III) macrocyclics whose a water molecule in the first coordination sphere can be removed under the conditions specified, offer support for the contention that the complex is composed of a planar ligand and two chloride ions surrounding a Sn(III) center:

The conductance studies were carried out in DMSO. As did the keto analog, the complex produced a colloidal suspension in ethanol and the reaction mixture was also colloidal. The nature of the solutions was determined by testing for the Tyndal effect employing a small laser. The conductance data were analyzed in a fashion similar to that used for $\text{Ni(acac)}_3\text{-Benzene}[\text{Cl}]_2$. The data confirmed that the complex was behaving as an electrolyte in DMSO, but was not completely dissociated into Sn^{2+} and Cl^- species, where L represented the planar organic ligand. This behavior is similar to that noted for the keto analog.

The molecular weight determination by vapor phase osmometry in DMSO was performed at Hewlett Packard labs by Dr. Bill Beck. An experimental value for 104 for the apparent

molecular weight fits reasonably well for a formulation of $\text{HfCl}_2\text{ZrCl}_2\text{SiCl}_4$ (0.5 mole)(2.5 H_2Si), the same formulation that fit quite well with the elemental analysis of the product as collected from the reactions and dried in vacuo at room temperature. If complete dissociation into four "particles" per mole of complex is assumed, the theoretical molecular weight would be 118. The possibility of having the solvent molecules included in the complex came as a result of the sample not being dried in vacuo over P_2O_5 at 70°C as was suggested. This oversight would have resulted in heating a sample as collected from the reaction mixture. The product was not subsequently dried before it was used since a time delay before analysis of up to one month had been indicated. The agreement with the suggested formulation is indicative of a correct assignment and even more importantly, it confirms unequivocally the assertion that the complex is dissolving as a monomeric compound that can dissociate into ionic species by displacement of the chloride ions in the axial positions by the solvent. Demonstrating that the complex was not polymeric was of major concern in view of the observed solubility data which could be interpreted in terms of a polymeric species. The demonstration of a monomeric complex which subsequently dissociated is in agreement with the conductivity studies which also indicated ionic species were formed in the CH_2Cl_2 solvent.

A NMR spectrum was run on many of the elemental preparations but no significant fragmentation patterns were obtained, although inlet probe temperatures to 350°C were employed. It

Table 1. Dissociation of Disaccharides (II) in DMF at 25.00°C

81 For dissociation Path $\text{ML}_2 = \text{ML}^{+} + \text{L}^{-}$

molality	$\alpha \times 10^3$	$\beta \times 10^3$	λ	$\lambda^2 \times 10^3$
DMF	1.552			
1	4.189	1.574	27.79	1.298
2	9.559	3.794	26.67	1.938
3	17.46	6.573	25.86	2.640
4	25.36	10.77	24.95	3.285
5	33.43	15.14	23.71	3.883
6	44.38	21.44	20.79	4.320

82 For dissociation Path $\text{ML}_2 = \text{ML}^{+} + \text{L}^{-}$

DMF	1.552	-	-	-
1	9.353	1.7821	33.46	1.122
2	3.898	1.837	33.33	1.178
3	17.46	1.483	38.88	1.513
4	25.36	3.387	47.38	2.245
5	33.43	7.532	48.41	2.793
6	44.38	28.117	41.48	3.274

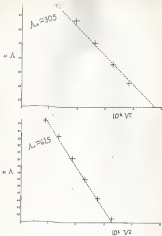


Figure 4. Dependence of current i on $V^{1/2}$ for (A) sample A-2305, (B) sample A-2615, both at 0.1 sec. pulse, pulse width = 100 μ s.

has been suggested that one of the ligands was surrounded by the quadridentate ligand and two chloride ions to form an uncharged species, the compound might exhibit some volatility. Subsequently, King¹⁷ indicated that if a complex is volatile to any degree, a parent peak is rarely, if ever found and it was the peak of major interest. Generally, one observes a splitting of the main radical from the remainder of the complex rather than an ionization of the complex. This phenomenon was not observed for these compounds, however.

An additional qualitative test was performed to confirm the existence of bound or potentially available chloride ions in the DMSO solutions. A precipitate of AgCl was collected by centrifugation after addition of a ten percent excess of AgNO₃ in DMSO (based on two available chloride ions per mole of macrocycle). The amount of AgCl recovered was less than one half of the theoretical amount, but the presence of available chloride ion was definitely established by these results.

Preparation of the free ligand was attractive for the same reasons as previously outlined for the intramolecular cyclization. The attempts to generate the aqueous ligand closely followed those for the bulk analog, viz., direct synthesis in a variety of solvents and under differing conditions as well as displacement of the metal from the preferred (M₂(macrocycle)Cl₂) by cyanide and sulfide. These experiments did not yield any free ligand, again stressing the tenacity with which the macrocyclic ligand is held by the metal.

As a result of infrared, ultraviolet and visible spectroscopy plus magnetic susceptibility, conductance and osmometer studies, the formulation for the complex in agreement with this data is a nickel(II) cation ion surrounded by a quadridentate acetylacetonate ligand with two chloride ions in the axial position.

9. Phthalate-Substituted C₁₂

The design and synthesis of [Phthalate-bisoxazolone]C₁₂ (VIIa) are conceived as an interesting and logical extension of the basic type of macrocycles discussed previously and prepared from one precursor. The retention of the strategy to employ the template effect, and more specifically to incorporate starting materials which contain a donor site not participating in the condensation step, made the basic approach very similar to that used for the two macrocycles (Va) and (Vb). The molecules chosen to build this macrocyclic complex are 2,6-diacylpyridine (DAP, VIII) and the dihydroformyl of DAP, 2,6-diacylpyridinedihydroformyl (DAPDH, IXa) which produce [Phthalate-bisoxazolone]C₁₂ (VIIa) when a cyclic condensation occurs.

The desired macrocycle has several noteworthy differences when compared to the two macrocycles (Va) and (Vb). [Phthalate-bisoxazolone]C₁₂ contains 14 atoms in the ligand ring which allows for the formation of two 5-member and two 4-member chelate rings. Other studies^{2,3} have shown that this is the optimum size ring to allow harsh raw transition metals to fit into without excessive strain being imposed on the ligand. It is noteworthy in this connection is the fact that many natural macrocycles offer a larger "bite" for the metal ion by incorporating all 4-member chelate rings in the complex. The contrasting behavior of natural systems suggests that the relative importance of size relationships between the metal and ligand have not been properly assessed or that other factors are operative.

3. General properties differentiating between the two

one macrocycle is the type of bonds incorporated into the complex via the starting materials. The zinc macrocycle (VIa) utilizes a hydrazine reactant which would contain a N-N single bond while the zinc macrocycles (VIb) and (VIc) use a starting material with a N-N double bond. It is true that, were the cyclic ligand be formed, formally different canonical forms can be written in which the N-N bonds contained in the two classes of macrocycles can be written as either a double or single bond. However, it is tempting to suggest the N-N single bond is the more important canonical form in the $[Ni-(\eta^5\text{-cyclopentadienyl})_2]$ while the N-N double bond canonical form is most important in the $[Ni-(\eta^5\text{-cyclopentadienyl})_2]$ and $[Ni-(\eta^5\text{-cyclopentadienyl})_2]$. X-ray data would provide a means for assessing the relative contributions of the various canonical structures but these determinations have not been made.

A third feature which differentiates the zinc and the zinc macrocycles is the types of groups contained on the periphery of the basic macrocyclic ring. The $[\eta^5\text{-cyclopentadienyl}]$ (VIa) and $[\eta^5\text{-cyclopentadienyl}]$ (VIb) contain a host of carbon-hydrogen groups, namely benzene rings, on the periphery of the complex presenting a reasonably non-polar shell. The $[\eta^5\text{-cyclopentadienyl}]$ contains less benzene rings on the periphery and has a more open structure which may permit solvent access to nitrogen lone pairs. This presents a shell that can participate in more polar interactions which should increase the solubility of the complex in polar solvents, a feature not characteristic of the zinc macrocycles.

Protonic molecular models were constructed of the proposed $[\text{N}(\text{acetoacetaldehyde})\text{Cl}_2]$ (VIIa). Surprisingly, the models indicated that there would be very little steric interaction in either $[\text{N}(\text{acetoacetaldehyde})\text{Cl}_2]$ (VIIa) or the corresponding analog $[\text{N}(\text{acetoacetaldehyde})\text{Cl}_2]$ (VIIb). If a truly planar configuration is assumed, the acetoacetaldehyde (VIIa) has the potential of some interaction between the methyl groups of the acetyl substituents and the hydrogen atoms of the pyridine moiety to which they are bound. That interaction, if it truly exists, should be small but would be totally absent if the methyl groups of DAP (VIII) were replaced by hydrogen atoms, thus leading to $[\text{N}(\text{acetaldehyde})\text{Cl}_2]$ if 1,4-pyridinedicarbaldehyde (IXa, IX) and its respective hydrates (XIXa, XIX) are used as starting materials. There exist a third possible macrocycle from this basic framework and is quite attractive in terms of investigating the steric interactions in a series of analogs. By choosing the combination of reactants as FDC (XI) and DAP (VIII) or the combination of DAP (VIII) and FDC (XI), a product would form in which only one-half of the methyl groups had been replaced by hydrogen. The diol macrocycle (VIIc) would allow a series to be studied in which a gradual change in steric interactions was effected in going from (VIIa) to (VIIb) to (VIIc).

With these differences providing an attractive rationale for the synthesis and study of the entire macrocycles (VIIa), (VIIb) and (VIIc), the synthetic procedures were developed for

attempted condensations. The general procedure for the preparation of $\text{Ni}(\text{acac})_2\text{bis}(\text{acac})$ (XIa) was again to be patterned after those found successful for $\text{Ni}(\text{acac})_2\text{bis}(\text{fl})_2$ (XIIa). The "template reaction" was tried first using ethanol as the solvent and adding a solution of DCPH (IXa) slowly to a refluxing ethanol solution of NiCl_2 and OAP (VIII) to which a drop or two of concentrated mineral acid had been added. The resultant product was the desired complex but the yield was quite small producing only 3-15 percent of the theoretical amount. It has been previously reported¹¹ that DCPH (IXa) forms a bis complex with NiCl_2 . The filtrate of the macrocycle preparation was shown to contain the DCPH NiCl_2 complex. In addition, a thin layer chromatograph of the filtrate was shown to contain unreacted DAP (VIII) starting material indicating that much of the DCPH (IXa) was tied up as another complex and that the OAP (VIII) was remaining in solution as an unreacted species. Thus, two modifications were employed in an effort to increase the yield of macrocycle.

First, the mineral acid catalyst was removed in case if this might increase the recoverable yield, the rationale being that the acid might be shifting the equilibrium amounts of the partially condensed product and the fully condensed Schiff base, thus making the bis hydrate complex and OAP more likely products. This alteration, however, resulted in no macrocyclic product separating from the solution even though the reaction conditions were identical to those incorporating the acid catalyst. A repeated experiment gave the

same results. Therefore, it was concluded that the mixture acid was essential for condensation leading to the macrocycle, although it was not tested further.

The second modification of the original method simply used an excess of the dihydrazone compound (XIIa) based on that needed to form the macrocycle. Using one third of a stoichiometric excess produced a fourfold increase in the amount of product collected. No further variations to maximize the yield of macrocycle were conducted since a sufficient quantity was available for further experiments.

The characterization of [Bis(acetylacetonato)(Cl)] was expected to parallel that of [Bis(acetylacetonato)(Cl)₂]. However, extensive efforts were in progress at the time to prepare one of the analogs, [Bis(acetylacetonato)(Cl)₂] (VIIb), as it was considered desirable to prepare the analogs in order to characterize the compounds simultaneously. Unfortunately, the complete series was not able to be synthesized. In fact, due to the efforts expended towards the syntheses, little characterization was performed on the unsaturated [Bis(acetylacetonato)(Cl)] (VIIa). The experiments used for the attempted preparation of [Bis(acetylacetonato)(Cl)₂] were postponed after the successful [Bis(acetylacetonato)(Cl)] synthesis. Thus, an ethanol solution of POCN (XIIb) was added slowly to an ethanolic mixture of Ni(DD) and POC kept at -80°C with the product being collected in a slightly different fashion. Addition of diethyl ether to the reaction mixture also precipitated the Ni(DD) synthon complex of Ni(DD). Therefore, instead of causing the macrocyclic

complex. After the use of a 100-gram (dry weight) amount, the solvent volume was reduced to approximately 10% of the original value and the methanolic is precipitated. The elemental analysis of the product did not conform to the pure $[\text{Si}(\text{acetoacetonato})_2\text{Cl}]$ and attempts were made to recrystallize the compound. Recrystallization from methanol did not produce the pure complex but the product did seem to agree with a formulation $[\text{Si}(\text{acetoacetonato})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}]$. Drying the sample in vacuo at 70°C over P_2O_5 did not produce the pure side complex and no corresponding formulation could be assigned. The analytical results for the attempts to prepare the side as well as the keto macrocyclic containing side linkages are as follows:

	C	H	N	Cl
Calculated for $[\text{Si}(\text{acetoacetonato})_2\text{Cl}]_n$	42.81	3.87	11.48	
Calculated for $[\text{Si}(\text{acetoacetonato})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}]_n$	41.1	3.98	12.8	
Found for product recrystallized:	41.43	3.34	12.14	
Found for product dried <u>in vacuo</u> at 70°C	41.93	2.74	11.17	
Calculated for $[\text{Si}(\text{acetoacetonato})_2\text{Cl}]_n$	48.36	4.49	18.74	13.14
Found for corresponding product:	48.33	3.93	18.98	13.15

Further modifications such as temperature variation, removal of acid and changes in stoichiometry were used in experimental attempts to isolate the pure $[\text{Si}(\text{acetoacetonato})_2\text{Cl}]$. Some of these procedures resulted in the isolation of the desired complex. The data collected in characterizing the $[\text{Si}(\text{acetoacetonato})_2\text{Cl}]$ (VtCl), in addition to the elemental analyses listed above, are presented and discussed next:

The infrared spectrum of $[\text{Ni}(\text{diacetonato})_2(\text{Cl})_2]$ (VIIa) is shown in Figure 7 and, following the approach of Nakamoto,¹¹ is expected and found to be quite similar to a composite of the reactants 2,4-diacetylpyridine (VIII) and 2,4-diacetylpyridine-dihydropyrene (IX) also shown in Figure 7. The absence of the CH_3 stretching bands at 1113 and 1368 cm^{-1} and the carbonyl mode at 1748 cm^{-1} is to be expected since coordination of these groups leads to an imine bond which in this instance is assigned to the 1688 cm^{-1} absorption on the remaining set forth for $[\text{Ni}(\text{acetonato})_2(\text{Cl})_2]$ previously.

The room temperature magnetic moment for $[\text{Ni}(\text{diacetonato})_2(\text{Cl})_2]$ was determined to be 1.83 B.M. using a diamagnetic correction of 1.64×10^{-4} cgs units calculated from Pascal's constants.¹² The value is an anomalous one and might be explained by a singlet-triplet equilibrium or the presence of different types of coordination geometry for $\text{Ni}(\text{Cl})_2$ ions within the crystal lattice structure. The observed value would correspond to roughly one paramagnetic $\text{Ni}(\text{Cl})_2$ ion to eight diamagnetic $\text{Ni}(\text{Cl})_2$ ions. A temperature dependence study might have resolved which species, if either, was responsible for the anomalous value of χ_{eff} . It might be reasonable to assume that the same factors causing the value of χ_{eff} in $[\text{Ni}(\text{acetonato})_2(\text{Cl})_2]$ (VIIb) and $[\text{Ni}(\text{diacetonato})_2(\text{Cl})_2]$ (VIIc) are also operative in $[\text{Ni}(\text{diacetonato})_2(\text{Cl})_2]$ (VIIa), since the basic ligand fields surrounding the metal are similar, but there is no experimental evidence to support this conjecture.

2,4-dinitrophenyl-
hydrazide (100 mg)

2,4-dinitrophenylhydrazide

2,4-dinitrophenylhydrazide

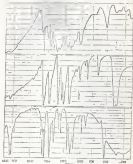


Figure 7

Infrared data

3. *Complexes of the Ni(II) Ion*

based on the starting materials and their possible reactions and the small amount of data collected on the final product. It is consistent to assign a formulation of a quadridentate ligand surrounding the Ni(II) metal ion with the two chloride ions occupying the axial positions. The system definitely warrants further study and is a particularly attractive situation since it is certain that the desired complex can be formed in sufficient quantity to study. Furthermore, there is good reason to believe that the anions discussed earlier, $[Ni(en)(malidomac)(Cl)_2]^{2-}$ (VII) and $[Ni(en)(malidohydroxymal)(Cl)_2]^{2-}$ (VIII) can be synthesized to allow a series of closely related compounds to be investigated, which should permit rather complete characterization of the complexes.

5. OXOBAS-III

The investigation that led to the discovery of the series of complexes [III] OXOBAS-III, where $M = Ni(II)$ or $Cu(II)$ and $X = Cl^-$, Br^- , SO_4^{2-} , NO_3^- or OH^- , was prompted by a series of observations. First, it was noted that the preparations leading to the formation of the aforementioned microcrystals (VI) and (VII) produced an intense purple color whenever $Ni(II)$ ion and OXOBAS (VIII) were present together in solution. Secondly, a microcrystalline substance could be isolated from a solution containing $Ni(II)$ or $Cu(II)$ ions and the diamine (VII). It was originally thought that the complex might be similar to the diacylglycidylalkylhydroxamate complexes (IX) studied by Stouffer¹¹ where two molecules of the tridentate hydroxamate ligand coordinate to give an octahedral complex. Since OXOBAS may function as a tridentate ligand, two OXOBAS molecules might coordinate to form an octahedral complex with the metal. However, the solid produced by the $Ni(II)$ or $Cu(II)$ and OXOBAS (VIII) reaction exhibited neither unexpected solubility behavior for complexes having structures similar to those of Stouffer's. The products were slightly soluble in acetone and could be dissolved in DMF and DMSO, but decomposed in the latter two upon solvation. No appreciable solubility was noted in water, methanol, ethanol, nitromethane or methylene chloride. In addition, on the basis of infrared spectra and visual appearance of the crystals, the product isolated from a 1:1 stoichiometric ratio of $Ni(II)$ to OXOBAS was furnished to be identical to that isolated from a 1:2 mixture. Furthermore, the dilute

of the 1:1 complex mixture contained a large excess of cobalt (III) starting material, consistent with the assertion that a 1:1 complex had been formed. However, it was difficult to envision the type of coordination that existed, since there didn't appear to be enough donor sites available to coordinately saturate the metal without involving a polymeric structure in which both nitrogens of the am-linkages would be coordinated. Another questionable feature of the proposed 1:1 complex was the consistently high values for the carbon, hydrogen, nitrogen and nickel analyses based on a formulation including two chloride ions, while the consistency of the elemental analyses indicated that a well-defined complex had been formed. This dilemma was resolved by formulating a complex (III) in which one proton had been lost by COOHAB, giving COOAB-S. Thus, the uninegative COOAB-S occupies three planar coordination sites with the fourth site being occupied by an anion introduced by the metal salt reagent. The existence of a neutral, square planar complex is entirely consistent with the solubility data where it was found to be insoluble in many polar solvents. The strongly solvating molecules DMF and DMSO dissolved the complexes, but the solution was accompanied by a change of color indicating that a change in the first coordination sphere had occurred. This may have arisen from a displacement of the anion by a solvent molecule, although these mechanisms were not characterized further. The lability to form an unstable complex from COOHAB and nickel(II)pyrazolone is consistent with the

proposed formulation. The weakly coordinating perchlorate anion apparently does not fill the fourth site to allow the formation of the neutral complex. However, the familiar purple coloration of the solution resulting from the mixture of nickel(II)glyoximate and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (VII) was taken as evidence for the presence of the metal complexed by the $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with perhaps solvent or water occupying the fourth site. All attempts to form a solid product met with dissociation of the complex present in solution into the separate starting materials. Therefore, it would appear that only a relatively strongly coordinated species in the fourth coordination site allows isolation of a stable solid.

Other systems have been reported which behave in a similar fashion. Brew and Lundquist¹⁷ prepared the β , β' -glyoxybisacetonates (XX) and the α -hydroxy-benzonitrile- β -naphthol (XIII) complexes of $\text{Cu}(\text{II})$. Both hydroxyl groups in these molecules were deprotonated giving a neutral complex with a metal to ligand ratio of 1:1. These ligands, like $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, can only coordinate to a given metal at three points. The authors originally postulated an unobstructed plane of coordination for the metal,¹⁸ a situation that seems highly unlikely in view of the X-ray data collected on metal complexes since their work in which it has been shown copper has usually have at least four ligand donor sites occupied. A much more likely mode of coordination would involve both nitrogens of the amine group functioning as donors. This is suggested later by Brew as a formulation for the many so

called "dye laser" coated by zinc dyes and metals. The metal fills the four coordination sites by using the three donors available from one ligand and then coordinates to the remaining one nitrogen of another ligand (XIII). Several examples¹¹ exist in which both nitrogen atoms of the azo group become donor sites to different metal centers. As noted previously,¹¹ an azo nitrogen is a relatively weak donor and usually doesn't coordinate unless a chelate ring can be formed. Consequently, the second nitrogen coordinated to the neighboring metal would be expected to be displaced by a strong donor such as is observed in the aforementioned complexes. When the 1:1 neutral complexes are recrystallized from pyridine or acetonitrile, some adducts are formed from the neutral "three coordinate" complexes. The solution color of the adducts is an intense purple, the same color observed for the OGGGG complexes.

A more closely related compound, 2'-hydroxybenzimidazole-5-naphthylamine (XIV) forms a 1:1 neutral complex with Cu(II) in which a proton is lost from each of the hydroxy and amino groups.¹² The resulting neutral complex was also considered to be only three coordinate and readily forms the pyridine adduct.

Azo compounds containing amino groups at both ortho positions of the benzene rings are the most closely related compounds and were studied and prepared by Price.¹³⁻¹⁵ Varying numbers and kinds of alkyl groups were attached to the ortho nitrogens. His studies indicate that the "acidity" of the amino protons are a result of a tautomeric structure

where the ano group is considered to be a hydrazone grouping or a shift of a proton. The corresponding tautomeric form for $\text{O}(\text{NH})\text{NH}$ would be:

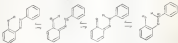


After coordination through the hydrazone form and loss of the hydrazone proton, a subsequent shift of electrons results in the molecule reverting to the ano form as in the following diagram:



The hydrazone process of the one tautomeric form is expected to exhibit acidic behavior. Beneshough, *et al.*,¹⁷ have shown that hydrazones derivatives of aldehydes and ketones can be titrated with tetrabutylammonium hydroxide in non-aqueous solvents. In fact, the titration may be used as a means of characterizing the compounds. Thus, the acidity of

a hydrazine species is definitely established. The evidence that the hydrazine tautomer really exists in some rare compounds comes from the work of Kelen¹⁰ and Kulinsky and Jones.¹¹ These authors studied the infrared spectra of ortho hydroxy substituted rare compounds and found evidence of N-H deformation bands which would have to arise from the tautomeric form. Coupled with this observation was the existence of carbonyl absorptions which led to the following postulated tautomeric structures:



The work of these authors showed the existence of the tautomers even in the solid state. It may be noted that the tautomeric equilibrium which exists in solution is normally shifted completely to one form or the other in the solid state. Therefore, the existence of tautomeric forms for suitably substituted rare rare compounds is also established which would render possible the mechanism set forth by Price¹² that coordination is effected through the hydrazine form with a subsequent loss of the hydrazine portion. Thus, what originally seemed like an unusual phenomenon, loss of a proton from an amine derivative, has a rather straightforward explanation according to Price.¹³

However, upon a closer scrutiny of the system, it seems that a simple acid-base equilibrium would lead to the same conclusion about the loss of a proton from the amine group. One could consider the nitrogen of the unsubstituted amine group to be quaternary nitrogen of the type $\left[\begin{array}{c} \diagup \quad \diagdown \\ \text{X} \quad \text{Y} \\ \diagdown \quad \diagup \end{array} \right]^+$, where X is the metal ion and Y is a phenyl or suitably substituted phenyl group. If both X and Y be electron withdrawing, due to inductive effects, the acidity of the "amine" will be greatly enhanced. For example, the following series of "ammonium" ions demonstrate the increase of acidity with the increase in the electron withdrawing nature of the substituents.

Name	Structure	pKa ¹²
ammonium ion	$\left[\begin{array}{c} \diagup \quad \diagdown \\ \text{X} \quad \text{Y} \\ \diagdown \quad \diagup \end{array} \right]^+$	9.2
anilinium ion	$\left[\begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_5 \quad \text{H} \\ \diagdown \quad \diagup \end{array} \right]^+$	4.6
3-nitroanilinium ion	$\left[\begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \quad \text{H} \\ \diagdown \quad \diagup \end{array} \right]^+$	-0.3
4-nitro- <i>o</i> -(4-nitrophenyl)-anilinium ion	$\left[\begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_3 \quad \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \end{array} \right]^+$	-6.3

pyridinium ion, pKa 5.2 2-phenylpyridinium ion, pKa 2.4



The comparison of pyridinium and 2-phenylpyridinium is pertinent to note that the substituent moiety has an electron withdrawing effect. The metal ion, M , would most certainly be considered an inductive electron withdrawing species as evidenced by the acidity of hydrated metal ions. Therefore, both M and R are electron withdrawing groups as




of the complexed OOMAB which should substantially increase the acidity of the protons of the amine group. The equilibrium:



is shifted to the right in the case of complexed OOMAB because the resulting uncharged complex is insoluble in the solvent system employed. However, the above inductive rationalization does not explain why there is only one proton lost from OOMAB. Why only one proton is lost from OOMAB is of some concern although a definitive explanation is not possible from this study. That inductive effects are truly operative in some crown complexes is exhibited by the removal of an amine proton from the complexed molecule under conditions

not sufficient to do so in the free ligand and in which
tandem structures are not possible." A.B.C The enhanced
acidity of the amine group which can be rationalized in terms
of an inductive effect should apply equally well to both
amine groups of $\text{Co}(\text{NH}_3)_6^{3+}$ once complexed. Naturally, the effect
would be diminished after the loss of the first proton since
the complex as a whole could be viewed as a diprotic acid.
This may explain why the second proton is not lost. Perhaps
the reason the second proton is not lost is that there is
not a neutral ligand of sufficient donor strength to fill
the fourth site of the metal coordination sphere. Or, possibly
the suggested mechanism set forth by Faine¹⁷ is operative
which only allows one proton to be lost due to the structure
of the hydrazine. It must be true that energetically the
change for the over-all process of losing the second proton
must be unfavorable, i.e., the gain in energy for each pro-
cesses as the increased metal-nitrogen bond strength and the
hydration energy of the proton is not sufficient to compen-
sate for the energy requiring process, one of which would be
the breaking of the nitrogen-hydrogen bond. While the above
rationalizations were attempting to focus on why the assumptions
worked out as they did, the fact is that there was only one
proton lost per molecule of $\text{Co}(\text{NH}_3)_6^{3+}$ under the conditions of
complexation employed in these preparations. Furthermore,
any of the explanations invoked to account for the acidity of
the molecule is consistent with the system.

The infrared spectra of the [Ni(CO)₄·H₂O] complexes are shown together with that of the uncomplexed liquid CO₂ in Figures 2 and 3. The spectra of CO₂ exhibit the characteristic¹¹ symmetric and asymmetric primary N-O stretching modes at 1380 cm⁻¹ and 1280 cm⁻¹, respectively. It would be expected^{11,12} that these absorptions should be lowered by 50-100 cm⁻¹ upon complexation. The spectrum of a [Ni(CO)₄·H₂O] complex becomes somewhat complicated in this region because of the loss of a portion from one of the main groups which effectively produces another type of N-O stretching frequency. As a first approximation, the nitrogen from which the portion is lost can be regarded as a secondary amine, , which should exhibit a single absorption. As a further approximation, the secondary amine should absorb at the center of the two split bands of the primary amine group. The absorption pattern for the [Ni(CO)₄·H₂O] shows essentially the pattern expected from these approximations, i.e., a split primary absorption at 1160 cm⁻¹ and 1130 cm⁻¹ with the secondary N-O absorption appearing at 1300 cm⁻¹. The N-H stretching bands for the [Cu(CO)₄·H₂O] complexes do not fit quite as neatly into the proposed pattern although it is evident that there is more than one type of N-H involved in the complex.

The assignment of the infrared absorption frequencies for the nitrogen-nitrogen stretching vibrations of an amine group is an area of uncertainty in the field of spectroscopy.¹³ Very little work has been devoted to this particular

DeMarzio¹⁰ and some questions remain in the reported literature because often times the molecules studied contained carbon-carbon or carbon-nitrogen double bonds which should be expected to absorb in the same region of the spectra. Leffers, *et al.*,¹¹ have studied a series of aromatic azo compounds and observed common absorptions at 1480-14 cm⁻¹ and 1570-15 cm⁻¹. They assigned the latter to the azo linkage on the basis that the absorption frequency should appear in the same region as the carbon-carbon and carbon-nitrogen double bond stretching modes. Herzberg¹² makes the assignment for the N-N stretching mode of azobenzene in this region while other workers^{13,14} have assigned the lower value to the azo stretching mode. This author agrees with the assignment near 1480 cm⁻¹ for the same reason as Leffers and his group. The free ligand OXALAC ought not be expected to show an infrared active azo absorption because of its symmetry and only in the 1575 cm⁻¹ region of the two possibilities suggested by Leffers, *et al.*,¹¹ does a band appear; therefore, no definite assignment was made.

The case of the infrared spectra of [M(OXALAC)-L]₂ are extremely similar as would be expected since the basic ligand portion is identical in all of the complexes. The notable exceptions occur when the ligand occupying the fourth coordination site of the respective metal contributes absorptions in the region studied. For example, the thiocyanate group, SCN, may coordinate to the metal via the sulfur or nitrogen atom. X-ray analysis has shown that first row

transition metals such as $\text{Cu}(\text{I})$ and $\text{Ni}(\text{I})$ tend to form π - π bonds whereas the latter elements in the lower rows favor the formation of σ - π bonds. Thus, it is expected that the $[\text{Ni}(\text{CO})_4\text{Ni}(\text{CO})_4]$ has a $\text{Ni}-\text{C}$ bond with the expected C-N and C-S bending vibrations occurring at 2150 - 2050 , 110 - 110 and 500 - 450 cm^{-1} , respectively.¹³ The $[\text{Ni}(\text{CO})_4\text{Ni}(\text{C}_6\text{H}_5)_4]$ complex exhibits a doublet at ~ 2120 cm^{-1} and a band at ~ 745 cm^{-1} (all neither of which appeared in any of the other complexes and is, therefore, assigned to C-N and C-S stretching modes respectively. It has been reported¹⁴ also that the C-S absorption can be split as was the case in $[\text{Ni}(\text{CO})_4\text{Ni}(\text{C}_6\text{H}_5)_4]$.

In the case of the $[\text{Ni}(\text{CO})_4\text{Ni}(\text{C}_6\text{H}_5)_4]$ complexes, a band appearing at 1770 cm^{-1} in the Cu complex and at 1765 cm^{-1} in the Ni complex, not evident in any of the other two complexes, is assigned to the ν - C stretching frequencies of the nitrate ion and is consistent with the reported literature.¹⁵ A splitting of the band would be expected when one of the oxygens is coordinated to the metal, due to a lowering of the symmetry of the ion. However, the occurrence of other ligand bands in this area makes shoulder bands on the nitrate absorption and the splitting, if present, cannot be assigned.

A coordinated anion complex would be expected^{16,17} to absorb around 1450 cm^{-1} and absorptions appear in this region for all of the $[\text{Ni}(\text{CO})_4\text{Ni}(\text{C}_6\text{H}_5)_4]$ complexes as a distinction was not evident in $[\text{Ni}(\text{CO})_4\text{Ni}(\text{C}_6\text{H}_5)_4]$. However, in addition to the ~ 1450 cm^{-1} absorption, some complexes also absorb in the 1400 - 1300 cm^{-1} region¹⁸ and an intense absorption at ~ 1180 cm^{-1}



Figure 8
Intra-day data

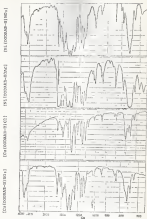


Figure 3

India: Red Data

observed in the IR spectra of this study which is most likely due to the acetate ion. Since the $[\text{Ni}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}]$, $[\text{Ni}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}]$ and $[\text{Co}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}]$ are not expected to exhibit any M-O stretching modes in the 400-600 cm^{-1} range, these complexes were used as guides for locating the additional bands assigned to other end-on stretching frequencies since the OOCCH_3 -O portion should be contributing all of the infrared absorptions in these complexes.

The ultraviolet-visible spectral data for the series $[\text{M}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}]$ is presented in Table 4. The similarity of the absorption curves and the extinction coefficients for the different complexes indicates a similarity of the solution species, whereas the similarity of the solid and solution spectra is taken as evidence for similar coordination geometry for the complexes in the two phases. The intense absorptions of the ligand charge transfer bands obscure the metal d-d transitions and consequently no assignment of coordination geometry can be inferred from the absorption positions in the ultraviolet-visible spectra.

Since previous studies by this author had shown that the complex (XII) could undergo further reaction in the presence of carbonyl compounds, specifically 2MF (VIII) or FOF (IX), the possibility of a reaction between the complexes and acetone was investigated, even though acetone does not generally undergo Schiff base condensations. A study of all the complexes prepared with the general formula $[\text{M}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}]$ showed that there was no observable change

change which occurred within 10 days at ambient temperature is either the ultraviolet-visible solution spectra or is the infrared spectra of the subsequently isolated solid complex from acetone solutions. The latter check on the infrared spectra was done to ensure that reaction between the complex and acetone didn't occur upon contact rather than gradually upon remaining in solution and thus not be noticeable in the ultraviolet-visible spectra.

The corrected magnetic susceptibilities, χ_M^0 , and the effective magnetic moment, μ_{eff} , for the zinc complexes are tabulated in Table 7. The measured values correspond to NiCl_2 and CuCl_2 in square planar coordination geometries yielding zero and one unpaired electron, respectively. There is apparently a small residual temperature independent paramagnetism in three of the nickel complexes as evidenced by values of 0.34, 0.34 and 0.36 for μ_{eff} . These values are not commonly encountered for NiCl_2 , however, it may well be because more diamagnetism was established for a given complex, the exact value of μ_{eff} was not computed and reported.

The molecular weights of the zinc complexes $[\text{N}(\text{OCCAAr})_2\text{Zn}]$ were determined by the vapor pressure osmometry technique employing acetone as the solvent and the results are reported in Table 8. It was of interest to experimentally determine the apparent molecular weight of these complexes to ascertain if the species present in solution was indeed a neutral complex with the anion coordinated. The experimental results verify that the complexes remain as monomeric neutral species,

Table 4. Dissociation-enthalpy, entropy data for $\text{Mg}(\text{COOAr})_2$ formation and melt.

a) Reaction spectra in systems					
	Compound	ν_A (cm)	$\epsilon_A \times 10^{-3}$	ν_B (cm)	$\epsilon_B \times 10^{-3}$
	[7a] (COOAr- β -Cl)	640	6.6	340	370
	[7b] (COOAr- β -Br)	620	8.2	345	338
	[7c] (COOAr- β -I)	615	6.5	340	348
	[7d] (COOAr- β -NO ₂)	620	6.8	345	348
	[7e] (COOAr- β -CH ₃)	630	ea. 50*	330	ea. 10*
	[7f] (COOAr- β -Cl)	525	8.1	330 ab.	345
	[7g] (COOAr- β -Br)	510	11	330 ab.	345
	[7h] (COOAr- β -I)				
	[7i] (COOAr- β -NO ₂)				
	[7j] (COOAr- β -CH ₃)				
b) melt spectra	[7a] (COOAr- β -Cl)	630		330	mixed continuous absorption
	[7b] (COOAr- β -Br)	640		330	below 400 cm for all melt spectra
	[7c] (COOAr- β -I)	638		335	
	[7d] (COOAr- β -NO ₂)	630		330	
	[7e] (COOAr- β -CH ₃)	620		345	
	[7f] (COOAr- β -Cl)	630		"	
	[7g] (COOAr- β -Br)	640		"	
	[7h] (COOAr- β -I)	640		"	

*Calculated solubility of compound presents with accurate determination.

even though the experimental error was significant in a couple of cases due to the extremely small solubility of the complexes in acetone. The ultraviolet-visible and infrared spectral data and the magnetic moments are in concert with the formulation of neutral, square planar complexes, also. An attempt was made to obtain mass spectra of the $[Pt(OAc)_2 \cdot 2Et_3N]$ complexes anticipating that the complexes might be sufficiently volatile as a neutral entity to observe a spectrum of sufficient intensity to draw some conclusions. However, Herz²¹ suggests that the molecular ion of metal complexes containing coordinated anions is seldom exhibited since the ionizing beam causes dissociation rather than ionization. It was anticipated that the position of any resultant peaks might allow identification of the original complex, however, sufficient intensity and resolution to draw valid conclusions were not obtained in any of the spectra.

The stability differences between a macrocyclic complex and a non-macrocyclic one is emphatically pointed out by comparing the resistance to acid hydrolysis of $[Pt(acac)_2 \cdot 2Et_3N]$ and $[Pt(OAc)_2 \cdot 2Et_3N]$. The latter is decomposed immediately upon contact with concentrated hydrochloric acid while the macrocycle can withstand several hours of contact at elevated temperatures.

The analytical results are tabulated for the $[Pt(OAc)_2 \cdot 2Et_3N]$ complexes in Table 2. On the basis of these results coupled with the infrared, ultraviolet and visible spectra, the

Table 7. Room-temperature dielectric permittivity ϵ' and susceptibility χ'' of $\text{P}(\text{DODAAH-B})\text{Cl}$.

Compound	ϵ' at 25.0°C	$\chi'' \times 10^{-5}$	Pearce's Correction at 10°C
$\text{P}(\text{DODAAH-B})\text{Cl}$	6.24	33.1	158.0
$\text{P}(\text{DODAAH-B})\text{Br}$	6	-28.8	148.2
$\text{P}(\text{DODAAH-B})\text{I}$	6.38	38.8	188.8
$\text{P}(\text{DODAAH-B})\text{NO}_2$	6	-21.8	158.8
$\text{P}(\text{DODAAH-B})\text{Cl}_2$	6.24	38.6	184.1
$\text{Ca}(\text{DODAAH-B})\text{Cl}_2$	3.78	1286	384.8
$\text{Ca}(\text{DODAAH-B})\text{NO}_2$	3.87	1648	513.5

Basic Structure of the Complex



+

+

Table II. Vapor phase refractive index calculations for $n_D(\text{DMSO-d}_6)$ in solution.

Compound	Exp't rotating in 10^3	Calc. $n_D(\text{DMSO-d}_6)$ in soln.	Exp't in air	Theoretical n_D in air
$\text{[H] (DMSO-d}_6\text{-d}_6\text{)]}$	3.2 3.3	0.348 0.310	1.46 1.48	1.47 1.49
$\text{[H] (DMSO-d}_6\text{-d}_6\text{)] in}$	3.5 3.7	1.14 0.37	1.46 1.54	1.47 1.55
$\text{[H] (DMSO-d}_6\text{-d}_6\text{)]}$	3.7 4.2	0.204 0.137	1.50 1.61	1.50 1.62
$\text{[H] (DMSO-d}_6\text{-d}_6\text{)]}$	3.2 3.6	1.37 0.33	1.15 1.45	1.15 1.45
$\text{[H] (DMSO-d}_6\text{-d}_6\text{)]}$	3.6 3.8	0.36 0.30	1.55 1.57	1.55 1.58
$\text{[H] (DMSO-d}_6\text{-d}_6\text{)]}$	3.6 3.8	0.33 0.30	1.46 1.48	1.47 1.49
$\text{[H] (DMSO-d}_6\text{-d}_6\text{)]}$	3.7 4.2	0.13 0.10	1.55 1.65	1.55 1.65

molecular weight distribution and the magnetic moment, the $(\text{M}(\text{O}=\text{N}=\text{O})_2-\text{R})(\text{X})$ complexes are formulated as square planar complexes composed of a tridentate, uninegative organic chelate coordinated through an amine and two amine nitrogen atoms with the respective amine coordinated in the fourth site of the plane.

The $(\text{M}(\text{O}=\text{N}=\text{O})_2-\text{R})(\text{X})$ complexes offer an attractive starting material for the preparation of macrocyclics. All that is needed to complete the organic ring around the metal is an appropriate dicarbonyl compound that also possesses a donor atom situated between the two carbonyl groups. Some possibilities which were briefly investigated are discussed further in Section X. One disadvantage of starting with the preformed $(\text{M}(\text{O}=\text{N}=\text{O})_2-\text{R})(\text{X})$ complex might be that an additional source of a proton must be present. This is normally provided by mineral acid addition and it may be that a given system is particularly sensitive to acid. However, the formation of $(\text{M}(\text{O}=\text{N}=\text{O})_2-\text{R})(\text{X})$ complexes that are well-defined broadens the scope of possibilities available to design and synthesize macrocyclic compounds.

Table 2 Analytical Data for [Fe(COCH₃AB-20-2)]

Compound	wt	nm	nm	nm
[Fe(COCH ₃ AB-8)Cl] calculated: found:	47.18 46.95	3.43 3.54	18.33 18.29	18.22 18.28
[Fe(COCH ₃ AB-8)Br] calculated: found:	48.89 48.47	3.17 3.36	16.81 16.89	16.78 16.48
[Fe(COCH ₃ AB-8)SCN] calculated: found:	47.69 47.42	3.38 3.29	20.75 20.82	17.90 17.84
[Fe(COCH ₃ AB-20-20) calculated: found:	43.42 43.33	3.34 3.48	20.10 21.48	17.44 17.88
[Fe(COCH ₃ AB-20-24Z)] calculated: found:	51.11 51.18	4.28 3.88	17.83 19.53	17.84 18.18
[Cu(COCH ₃ AB-8)Cl] calculated: found:	46.48 46.71	3.57 3.43	18.06 17.80	20.48 20.37
[Cu(COCH ₃ AB-8)Br] calculated: found:	48.89 49.68	3.19 3.31	20.80 20.74	18.88 18.88

1. Early Synthetic Biology: Condensing Reactions

Exploiting the criteria developed in the introduction for synthesizing planar, quadrilateral and conjugated macrocyclic systems, the first attempts involved the condensation of two more bifunctional molecules to build the organic ring. Most of the reaction schemes involved the formation of imine linkages. These could be most easily formed by the reaction of a primary amine with a carbonyl group, either an aldehyde or ketone. One of the first schemes shown lends itself to quite a variety of starting materials. A molecule originally containing adjacent carbonyl groups was reacted to form the dihydrazide compound (XXIII). This gave a bifunctional molecule containing pendant NH₂ groups which were independently shown to be capable of condensing with carbonyl groups even though it was a hydrazine function. At least one other worker²⁰ has also condensed the hydrazones and carbonyl functions to prepare lipids. Of course, one of the classical organic qualitative analysis tests for carbonyls involves the use of a hydrazine group to prepare derivatives for identification purposes.¹⁹ Therefore, there is adequate literature to demonstrate the feasibility of incorporating the NH₂ groups into a condensation reaction. The dihydrazones could be formed from several carbonyl compounds which would produce different dihydrazones (XXIII). It was anticipated that a dihydrazone such as glyoxal-dihydrazone could be reacted with two additional α -dicarbonyl molecules. This could lead to structure (XXIV) written in the conformation that would allow

for condensation is 1 mole/l., the product could then be reacted with an α -diamine such as α -phenylenediamine (XCV), so since the organic rings this latter step to be attempted in the presence of a metal. Bush and coworkers⁶ had shown that the presence of a metal was often essential in the preparation of synthetic metalloporphyrin structures. This fact was originally termed a "template" effect. The "template" effect was later defined and divided into two modes of interaction between the metal and organic molecules.⁷ At any rate, it was thought that addition of the metal salted the organic molecules so that cyclization might proceed in the proper fashion. The use of the metal was not essential in this scheme as the desired porphyrin (XCIV) was not insoluble. The primary attempts were directed toward a condensation of glyoxal dihydrazones (XCVIa) or benzoyldihydrazones (XCVIb) with two molecules of either glyoxal (Ia) or bis-acetyl (IVb). The most general procedure involved the addition of a solution of the dihydrazones to a solution of the α -diamine. Polymerization, or probably more correctly the formation of oligomers, even though the two terms will be used interchangeably to indicate the occurrence of multiple linear condensation, proved to be a major problem with this scheme; a number of parameters are involved in this particular reaction scheme and several modifications were used in an effort to minimize the oligomer formation. These variations included 1) changing the temperatures of the reaction from ice bath

to refluxing acetic acid, 3) increasing the concentrations of reactants as well as the frequency of addition, 4) increasing the amount and changing the type of catalysts employed as well as trying the absence of any added catalytic material and 5) changing the time allowed for reaction from quenching immediately after mixing of the reactants to times of 16 hours. However, all of these approaches led to the formation of yellow solids which were insoluble in most polar and non-polar organic solvents as well as water. The infrared spectra, although not extensively studied, showed only a small absorption in the 1700 cm^{-1} region indicating that free carboxylic were not a major component of the product as desired. The most conclusive data as to the composition of the products resulted from the mass spectral data. These showed numerous peaks at higher m/e values than the desired trimer indicating that material of a higher molecular weight was the primary product. Interchanging other dihydrazones such as benzilidihydrazones (BDHHz) also did not lead to any successful isolation of the preferred trimeric compound.

The next approach to the synthesis of cyclic liquids capable of further condensation was to avoid macrocycles by using the same starting materials as previously, but in reverse stoichiometry. Condensation of two molecules of the dihydrazones to one of the α -diketone would result in structure (XVIII). The cyclic ring could be completed in this case by the addition of a dicarbonyl compound. Again, polymeric material was the main product and adjustments in the reaction

conditions did not allow isolation of the desired triazene. Techniques used in the isolation attempts involved recrystallization and solvent extraction in addition to thin layer and column chromatography. An in situ incorporation of CuOTf was attempted since the precomplexed portion of the macrocyclic ligand was unable to be isolated. The various combinations of starting materials employed in the previous experiments were again tried, likewise reagents in stoichiometric mixtures. The idea was to add a metal ion to the combined mixture of condensing reagents soon after they had been mixed. Busch² and co-workers have utilized successfully this procedure in the synthesis of several macrocyclic systems. The delayed introduction of the metal ion may allow the metal ion to operate through the thermodynamic template effect, although it is possible that the metal might be operating the organic molecules and then be operating through the kinetic template effect also. Accordingly, a delay of approximately five minutes passed before the metal was added to the mixture of reacting components. Two variations were used from this point in the experimental scheme. The first variation was to attempt the isolation of the metal complex of the desired triazene (CuOTf), then to react this product with the chosen α -diamine to complete the macrocyclization. The isolation of the desired complex was rendered impossible by the isolation of several other metal-ligand products, one of which was likely to be the bis- α -diamine complex as indicated by comparison of the infrared spectra of some reaction product with an authentic

sample. Failure to isolate the desired cyclic ligand compelled us another approach, because it was assumed that some of the desired trimer complex product had been formed in solution; accordingly, the ring closing carbonyl was added directly to the reaction mixture. Numerous changes in reaction conditions were tried after isolation of the final macrocycle was not achieved but in all cases the isolation techniques failed.

After an extensive alteration of reaction parameters failed to produce macrocyclic complexes from the initial reactants chosen, it was apparent that some basic changes must be introduced in the reactive species. In an effort to alleviate some of the polymerization problems encountered above, but still focus on the formation of a new linkage, a new approach was attempted. The new method incorporated bifunctional molecules in which there was a difference in the reactivity of the two groups. Continuing with the reaction between amines and carbonyls, it seemed best to vary the reactivity of the carbonyls. Reasoning as the carbonyls was due mainly to the fact that the nitrogen atom in the starting molecule is limited to one bond other than the two bonds containing hydrogen atoms needed for the condensation reaction. This other bond must be joined to an atom which will become a part of the basic ring. This atom would have to have groups bonded to it to alter the reactivity of the primary amine function and this places the groups used for altering the reactivity of the amine at least one site removed from the TN moiety. A carbonyl is capable of

having substituted groups attached directly to the carbon atom containing the doubly bonded oxygen. This allows substituents in closer proximity to the carbonyl which might allow a greater alteration of reactivity. Replacing the groups attached to the carbonyl has additional advantages. Some of substituents would be incorporated into the basic ring of the macrocycle. Too, the substituent group would be pointed away from the basic macrocyclic ring allowing for minimal steric hindrance if bulky groups were chosen for bonding to the carbon. However, a slight disadvantage from the steric requirements of carbonyl substitution is that the substituent is held in the same plane as the carbon atom to which it is joined and the nitrogen atom ultimately used for macrocyclization. This poses the potential problem of the groups causing some deviations in the planarity desired for the macrocyclic ring.

The molecules chosen to provide a difference in the reactivity of the two carbonyl groups were pyruvaldehyde and phenylglyoxal, structures (IVb) and (IVc) respectively. It was anticipated that the greater reactivity of the aldehyde group would provide enough differentiation in the reactivities of the two carbonyl groups that the step-wise condensation would halt at the trimer (XIV) and at least reduce, if not retard completely, the polymerization.

The formation of a trimer containing one dihydrazones unit and two diacarbonyl units was still the primary goal, structure (XIV). This product might then be closed by reacting with a diamine molecule as planned in the previous

reaction mixture. Small amounts were directed at preparing and analyzing the ligated triene.

A yellow solid was obtained by slow addition of a solution of the dihydrazine to a solution containing a large excess of phenylhydrazine. The product was insoluble in water and most common organic solvents. An infrared spectrum of the product contained only a small absorption in the 1740 cm^{-1} region and the mass spectrum showed peaks at much higher m/e values than that of the desired product, both observations indicating that polymerization had taken place. Variations in the temperature of the reaction, addition rate, and length of reaction produced products very similar to above isomer as the polymeric character is concerned.

In this latter approach as well as those described previously, variations in acid catalysis were tried. If no additional proton acid was placed in the reaction mixture, the system reacted at a moderate rate as evidenced by the appearance of a yellow color within approximately one half hour. If extra acid such as one drop of 3N hydrochloric is added, the formation of intense yellow coloration and solid appears almost instantaneously. This observation is consistent with the proposed mechanism discussed in the Introduction, however, the differences in rate are rather drastic. The product isolated was similar in both the catalyzed and uncatalyzed cases.

One additional variation used involved an attempt to isolate a one to one ligated product, structure 100VIIb, to

this procedure, very dilute solutions, neutralized, of 10^{-2} M is 18% of the dihydrazones and phenylglyoxal were simultaneously added to a flask under varying temperatures and addition rates. Again, these reactions produced polymeric compounds similar in composition and properties to the IVI which was used in the previously mentioned experiments.

Because a direct synthesis of the precursor ligand (XIII) was unsuccessful, an *in situ* preparation was attempted. Procedures similar to those employed for the *in situ* synthesis using symmetrical starting materials were followed. One of the template effects would undoubtedly be operative during the reaction sequence to produce the desired product, structure (XIII) with the metal complexed. This precursor might require coordination of carbonyl groups to the metal if a one to one ligand to metal ratio was prepared. Although it is known that the strength of a carbonyl-metal coordinate bond is weak,²² the chelate effect of the ligand as a whole might enhance the stability of the product and render feasible its isolation. The reactions attempted in which the glyoxal-dihydrazone was added to a solution of a metal and phenylglyoxal in which the reactants were present in the stoichiometric ratio of 1:1.4, respectively, yielded no isolable product. In other trials, the metal ion in solution was added to a previously mixed solution of the glyoxal-dihydrazone and the phenylglyoxal, where the reactants were present in a 1:1:2 stoichiometric amount, and again did not result in the quantitative isolation of a complex. Bisoxalyl-dihydrazones and pyro-

aldehyde were substituted as additional trials. The metal ion chosen to provide the template effect was varied between Cu(II) and Co(II) , both as the hydrated chloride salt. It was proposed that the acetoxy groups did not provide sufficient bond strength to allow isolation of Cu(IV) although it might be present as a solution for finite periods of time. If the complex Cu(IV) was present in solution, it could be reached and removed from solution with a diamine compound to close the liquid structure. The results of reactions tried by adding a diamine such as $\text{p-phenylenediamine}$ (XIV) after the metal, the alkydienes and the phenylglyoxal had been reacted by one of the sequences outlined above produced a different product than when the diamine was absent. However, a simple macrocyclic complex could not be isolated from any of the trials. The product isolated by addition of the $\text{p-phenylenediamine}$ proved to be the $\text{p-phenylenediamine}$ complex of the metal. A framework molecular model of the proposed cyclic product showed that considerable steric hindrance is present and might have been the reason that no macrocyclic product was formed, rather than the fact that none of interest was present in the completed state.

Unable to prepare the desired ligands by any of the previously described procedures, the author directed attention to another type of molecule to condense into linear containing molecules. Macrolists were desired which could condense but which would limit the possibility of polymerization. The type of molecule chosen possessed only one acetoxy group

capable of cyclization. The α -hydroxy-carbonyl group of the molecule was rendered unreactive for imine formation¹¹ by previously forming the acetal (XVIII). A decision was made to synthesize trimers of the type (XIX) which would then be incorporated into a final cyclic ligand. The acetal can be hydrolyzed back to the carbonyl by a peroxo acid.¹² It was postulated that a metal ion might also hydrolyze the acetal and thus give (XXIV) which could then be condensed with a diamine compound to complete the cyclization. The postulated hydrolysis of the acetal by the metal ion was borne out in the following work but the desired macrocycles were not isolated.

Most of the experiments involving reactants containing protected aminoxylo utilized thioacetylenes (XVIII, XXIX); glyoxythioacetal (XXVIII, XXX), pyruvathioacetylenes (XXVIII, XXX); or β -oxothioacetaldehydeacetal (XXXI, XXXII).

XXX was reacted with 50% (XIII) in the presence of NiCl_2 hoping to generate (XXIV) which could then react with a diamine to close the cyclic ring. Addition of γ -benzylated diamine or ethylenediamine after the XXX, XXX and NiCl_2 were allowed to react for five minutes in the ratio of 1:1:2 caused the formation and subsequent isolation of the diamine complex of (XXIV). The XXX was extremely difficult to prepare and further investigation was halted due to the lack of compound and the unfavorable results noted above.

XXX (XXXII) proved to be much easier to prepare and several experiments were designed to try to incorporate this moiety into part of a ligand structure which would sublimate in a macrocyclic product. No reaction was observed when condensation of two molecules of XXX (XXXII) with 1 molecule

of COM (XIII) was attempted in methanol media, unless a drop of concentrated hydrochloric acid was present. The conclusion that no reaction had occurred was based on the results of thin layer chromatography of the reaction mixture and the starting materials. No apparent new spots were observed from the reaction mixture while the spots present corresponded to starting materials. It was suggested that perhaps the silicon coating on the plate might be hydrolyzing the protective groups¹¹ and therefore that the R_f values would actually corresponded to the respective diacryloyl compounds. This possibility was not checked extensively as it didn't seem to be critical whether the absolute composition of the spots were known, but simply whether any of the starting material had been consumed to form a condensation product. Positive results were beginning to appear by another synthetic route and further checking of this point did not seem warranted under these conditions.

The product formed in the presence of acid catalysis was extremely similar to the products isolated from the reaction of COM with unprotected diacryloyl compounds. This was presumably due to the hydrolysis of the acetal groupings and then polymerization of the resulting bifunctional molecule. The acid addition was used in order to help catalyze the pinic formation from the "free" carboxyl of BACC and ester groups of COM. However, the fact that no condensation product was observed in this case without acid and the apparent unreactive nature of BACC in many of the experiments

attempted in this laboratory points to the fact that the "free" carbonyl is not reactive towards base formation in the absence of a catalyst. Unfortunately, the catalyst to increase the rate of "free" carbonyl reaction apparently also hydrolyzes the metal groupings leaving a path for polymerization. Consequently, no desired macrocyclics were produced by the use of EtOH as a building block of the ligand.

Aqueous hydrazine was added to MgCl_2 and no apparent reactions took place even at elevated temperatures. A reaction of EtOH with COCl_2 was tried at a 1:1 ratio in methanol with no reaction observed at various temperatures. A metal was introduced into the COCl_2 and metal reaction in an effort to produce (XIII) with the driving force possibly being the formation of a tetradentate ligand if coordination of the "free" carbonyl occurred and then the metal grouping was subsequently hydrolyzed by the metal. The metal addition produced some of the metal ion complex (XII) but none of (XIII) was isolated. One further modification was tried by adding O_2 (XIII) to the COCl_2 , EtOH and metal mixture. It was hoped that the O_2 would combine with any of (XIII) that might be present to form the closed macrocyclic complex (XIII). This would have amplified the kinetic template effect, however, the template effect apparently was working with a different ligand system because the product isolated was the O_2 tetrameric macrocycle (XIV) reported by Bush and his coworkers.²

It was suggested¹³ upon inspecting the results of the experiments incorporating protected molecules that steric interactions might be causing the corrective nature of the protected molecules. Framework Molecular Models at MIT (XIIIa), OSA (XIIIb) and PPA (XIIIc) definitely demonstrated the congestion present in these molecules that might prevent attack of the "free" carboxyl carbon by a nucleophile. More detailed considerations of the steric might or might not reveal that this is the case but the explanation is at least consistent with the results observed by this author.

In view of the inability to obtain condensation products from LMS while still containing a protected carboxyl, it was decided to try some other protected molecules. The compound OAB (XIVa) was an attractive molecule to use as a building block in macrocyclic ligand design. However, it had the serious drawback of reacting with itself. In the absence of metal ions, it forms the trimer (XIVb) while in the presence of metal ions, it forms the tetrameric macrocycle (XIVc). This work had shown that these reactions tended to predominate even in the presence of other potential condensing reagents. The attractiveness of using the OAB in constructing the ligand led to attempts to modify the OAB to prevent the self condensation. The best route seemed to be the preparation of the ester of OAB (XIVd). This would leave the ester group free to condense with carboxylic groups on other molecules but presumably not with the protected carboxyl of other OAB molecules. There was some question about the purity of (XIVd),

The protected diol was prepared by mixing the acetal of 2-nitrobenzaldehyde, then reducing the nitro group to the amine by hydroxylation over a platinum catalyst. This reaction was due to the isomerized isomerization of the acetal process obtained on the one hand. However, thin layer chromatography showed only one spot for the compound as prepared. The material was used as collected when attempts at distillation resulted in decomposition of the oil.

Surprisingly, a condensed product was not obtained when the diol acetal (XIII) was mixed with aqueous glyoxal under various conditions. The protected diol was also mixed with bisoxyl (IV) to attempt a condensation although there was no opinion about obtaining a product, since there apparently was no reaction with the more reactive carbonyl functions of glyoxal. No product was isolated and it was decided to employ the template effect by adding a metal ion to the mixture of the diol acetal and the dicarbonyl. Reaction occurred when the metal was introduced, however, the product was the diol octamer (XIV). It was becoming apparent that the Schiff base formation was not as spontaneous in many cases as had been hoped and that changing conditions to favor the condensation also favored the acetal cleavage. The removal of the protecting groups then left a pathway for other undesirable reactions, such as polymerization, to take place. One additional experiment was tried on the chance that the two reactants might condense under conditions not destroying the protecting groups. In this case, XIII and XIV were mixed in a stoichiometric ratio to hopefully form the dimeric compound.

This did not prove necessary, even with metal addition.

Another molecule chosen as a potential building block of a macrocyclic ligand was diaminomaleonitrile (XXIII, 544/1). This molecule appeared to be favorable because it contained two primary amine groups capable of Schiff base formation and would also provide conjugation through the double bond joining the carbon atoms which bore the amine groups. The conjugation was possible without using a benzene ring to incorporate the double bond joining the adjacent amine groups. It was hoped that the use of this smaller molecule with the polar cyanide groups would prevent less steric hindrance in certain macrocycles and might improve the solubility characteristics of the final cyclic complex in polar solvents. The DMS was prepared by the method of Henderson, op. cit.,¹⁸ which proved to be quite lengthy and sensitive to apparatus and catalyst surface condition while the starting material was highly poisonous hydrogen cyanide gas. The product as now commercially available at a reasonable price from Terra Marine Research of California, no desired product was isolated when condensations were attempted between DMS and diacetonyl compounds (glyoxal or bisacetyl) under various conditions and acidities. Linear polymerization and cyclization to form six-membered rings (XXIV) were the main reactions. Separate experiments attempting to form the bis or tris DMS complexes of Cu(II), Ni(II), Fe(II) and Co(II) suggested that the DMS compound was rearranging or becoming oxidized in some fashion during experimentation as evidenced

compounds that various hydrazones were produced. This work was discontinued with this material since the instability of HAN simply compounded the fact that many other reaction routes were possible in addition to the desired condensation.

Another early attempt at macrocycle synthesis involved a different type of reaction. This approach used the reaction of formaldehyde with amines. A review by Fetter¹⁴ on this subject indicated that formaldehyde had the capability of joining two primary amine groups through methylene linkages (XHO). This occurred in preference to the formation of two separate amine functions which is possible in principle because formaldehyde contains a carbonyl group and could undergo a Schiff base condensation. The formaldehyde reaction is not limited to primary amines, but can also proceed with secondary amines, the only requirement being that the nitrogen atom contain at least one hydrogen. The formaldehyde-amine reaction was employed to join the amine groups of a previously prepared bis glyoxalaldiphenyl complex leading to a formation as shown in (XHOPI). Although the resulting macrocycle would not have been conjugated, it might have been possible to introduce some additional unsaturation into the complex by selective oxidation after it was isolated, since this procedure has proven successful previously.¹⁵

The expensive attempt to employ the formaldehyde-amine linking process did result in some type of reaction taking place. The procedure followed was that of preparing the well-characterized bis hydrazone complexes of dipositive

silver) complex, iron or copper is solution without liberating them. This solution mixture slowly was contacted with a stream of aluminum and then had a stoichiometric excess of deaerated aqueous formaldehyde added after which the reaction mixture changed from a colorless slurry to a dark red-brown solution. Reducing the volume of the final reaction mixture did not yield any visible precipitate until the last few drops of solution were left. The precipitates produced were not of a crystalline nature and appeared to be amorphous as viewed thru a microscope. However, by accident it was noted that the residue from the reaction using $\text{Cu}(\text{Cl})_2$ as the metal ion produced an intense deep purple color when treated with sulfuric or perchloric acids. This particular observation appeared to be quite unusual in view of the acid sensitivity of the bis hydrazine complexes.^{11,12} The color formation on treatment with one of the two acids coupled with the observations of the color change of the reaction mixture, the physical differences between the solid isolated and the bis hydrazine complex, and finally the fact that the infrared spectra of the solid isolated contained only small absorptions in the 1400-1500 cm^{-1} region were all taken as evidence that reaction had occurred in the system. The colored complex formed on the addition of sulfuric or perchloric acid was stable for many days and was pH dependent. The color could be changed to a green by addition of solid sodium bicarbonate and raising the pH of the solution to a value somewhere less than one. The color changes were reversible, however,

[and stability] of the epinephrine was not as great and a reduced intensity of purple color was obtained if the green solution was left standing for over one half hour before the addition of concentrated sulfuric or perchloric acid. Epinephrine acid treatment of the solid resulted in a green colored solution, while addition of nitric acid caused decomposition of the material upon contact. It would be entirely consistent with these results that some type of acid-base phenomenon is operating in these systems. There are many examples of such compounds used as dyes in which the colors are quite dependent.¹⁴ Most effort was devoted to the study of this phenomenon and consequently little work was directed towards the isolation of the macrocycle from the original reaction mixture. Even though the ultimate goal of isolating the macrocyclic complex (IXVII) was not accomplished, this particular area of macrocycle investigation seems, in retrospect, to contain some promising observations and may well prove to be quite fruitful if reopened to investigation. This would seem to be especially attractive in light of the work of Carter^{15,16} in which a new macrocyclic ligand was accidentally formed by the coupling of two amino groups by a carbonyl containing compound.

One other area which deserves closer scrutiny and which was investigated along this line would be the use of quinoxaline formaldehyde as the reactant with a but hydrazine complex. This was attempted to presumably alleviate the toxicity of sodium water which it had been theorized might be causing

and ammonia in the isolation of the acid generated purple complex and confirmed noted that water seemed to decompose the red-brown precipitate created by evaporating the hexahydrate-formaldehyde reaction mixture. Therefore, dry gaseous formaldehyde was generated and passed over the solid hexahydrate complex. A reaction appeared to take place as evidenced by a color change, but the majority of the effort was focused upon the species created by the acid treatment of the reaction product.

Thus, the previous attempts did not result in isolation of the desired products even though the methods looked feasible on paper. Perhaps with a bit more persistence, some of the products might have been recovered in small yields. Nevertheless, synthetic macrocyclic ligands continued to appear in the literature. In almost every case, the synthesis had been carried out in the presence of metal ions. Either the metal seemed to be essential for product formation or to greatly enhance the yield. Consideration of the successful preparations reported made it apparent that a specific feature of the condensing molecules was recurring in these systems even though not explicitly pointed out in any of the articles. Namely, at least one of the reagents derived in the condensations contained a donor atom(s) not involved directly in the condensation. Furthermore, the additional donor(s) was situated between the reacting groups contained in the same molecule. The utility of this feature is most likely connected to the template effects caused by the metal ion. The sub-

placing donor could conceivably contribute to the total and help the molecule in the appropriate orientation and vicinity of the other molecule(s) until reaction occurs completing the ligand cyclization (see Introduction).

The description of the work utilizing the postulated concept above is included in the preceding subsections as it represents a different approach and resulted in the isolation of some of the desired products. The results of this work tend to support the donor postulate although no kinetic data was taken to attempt a proof. However, it is also obvious that simple incorporation of molecules with this property into a synthetic scheme is not sufficient to assure production or isolation of macrocyclic compounds.

CHAPTER II.

EXPERIMENTAL:

ANALYSIS:

Spectrometry-Infrared and NMR spectra in the visible and ultraviolet regions were obtained using a Cary Model 14 or a Beckman DU-7A recording spectrophotometer. NMR spectra were obtained by using a cyclo mill spread on a glass suspended in the beam. Infrared spectra were obtained using a Perkin-Elmer 121 sodium chloride Spectrophotometer and a Perkin-Elmer 121 double beam Infrared Spectrophotometer. All infrared data were calibrated against polystyrene. The pressed potassium bromide pellet technique was used. NMR spectra were obtained on Varian Associates Model A60 and Model B60 nuclear magnetic resonance spectrometers using tetramethylsilane as a reference. Mass spectra were obtained on a Hitachi Perkin-Elmer Model RM 45 spectrometer.

Vapor pressure osmometry-The apparent molecular weight determinations were performed in this lab by using a Beckman, Inc. Model 500 vapor pressure osmometer except when the solvent employed was dimethyl sulfoxide. Repeated attempts to stabilize the instrument for the calibration procedure with DMSO were unsuccessful even though other solvents were successfully used before and after this work. It turns out that DMSO is a particularly difficult solvent to use in this type

Measurements of viscosity—Rotational—Brookfield's apparent viscosity meter. However, one person in this study had apparently been able to get reliable readings on a DSO on at least one previous occasion. Dr. Bill Beck of Benedict Parkard, Avondale, Pa., offered to collect data on two samples dissolved in DMSO and performed the work at an operational temperature of 40°C using a Benedict Parkard model 102 B Vapor Pressure Oscillator in conjunction with a Benedict Parkard Model T127 strip chart recorder running at 0.05 in./min.

High-vacuum distillation—A Thomas Hoover "end-cell" capillary melting point apparatus was employed; the temperatures are uncorrected.

Analysis—Carbon, hydrogen, and nitrogen analyses were performed by Gallowith Laboratories, Inc., and Functional Group Research, Inc. Metal analyses were initially obtained by using a Perkin-Elmer Model 2400 atomic absorption spectrometer. All samples were analyzed in aqueous solutions after digesting the complex almost to dryness in a 1:1 mixture of concentrated nitric and perchloric acids. The metal analyses reported herein were performed by the EDTA back titration procedure described in the experimental procedures section.

Centrifuge—Centrifugation was performed on an International Equipment Co. clinical centrifuge Model CL. For sample sizes larger than 10 ml or when greater speeds were desired, a larger Model 8W110 from the same firm was employed.

Conductance equilibrium—Conductance measurements were made in a Kraus type 105 ml conductance cell supplied by Beckman.

The coil constant was 0.1312 cm^2 and all solutions were contained/forced by an internal magnetic stir bar. A Jern-Holm type conductivity bridge previously described¹¹⁴ was employed and the measurements were made at $10 \pm 0.5 \text{ Hz}$. The constant temperature bath was approximately 34 gal. in size and equipped with two circulating pumps. The bath was filled with transparent transformer oil and regulated to $25.00 \pm 0.05^\circ\text{C}$ by a Yellow Springs Instrument Co. Model 72 temperature regulator. The units of conductance obtained were $\text{ohm}^{-1}\text{cm}^{-1}$ specific conductance.

Vacuum oven-drying was done under vacuum at elevated temperatures with a National Appliances Co. Model EAM vacuum oven.

Zero apparent-Nernst electromotive force were determined by the Gouy method using equipment described previously in greater detail.¹¹⁵ The magnet used was a Varian Associates Model W-40000 equipped with four-inch cylindrical pole pieces, separated by an air gap of 1 1/2 inches. A Varian Associates Model V-2111-A current regulator was used to provide a constant current ($\pm 1 \times 10^{-1} \text{ amp}$) and was powered by a Varian Associates Model V-2100-A power supply. The maximum field strength obtained was 5712 gauss/cm. The negative field was calibrated using mercury(II) tetrachloroaurate(III).¹¹⁶ The system and temperature control apparatus used were of the basic design of Pippas and Wyble.¹¹⁷ Temperatures between 15° and 400°F could be maintained within ± 0.1 degree as determined by a platinum resistance thermometer. The sample

sample was in a cylindrical block of quartz, approximately 3.5 cm inside diameter, 7 cm in length which was sealed at one end. Approximately 1 g of oil was used for containing the sample volume. It was suspended in the cryostat from a stainless steel balance by a gold chain attached to a tapered Teflon plug. The diamagnetic correction of the tube was measured as a function of the temperature between 80° and 400°. A Mettler Model 8-6 semi-micro balance of 0.01 mg sensitivity was used to measure the force exerted by the magnetic field upon the sample. Most weighings of laboratory chemicals were performed on a Mettler Analytical Model 8 balance.

Chemicals

Reagents—Unless otherwise specified all chemicals were commercially available reagent grade and were used without further purification.

Water—Distilled water used for all solutions was obtained by distillation of deionized water from alkaline potassium permanganate in an all glass apparatus. It was stored in pyrex glass bottles until to use.

2,6-Dichloroquinonechloranil (DCUQ)—A modification of the procedure of Carlson, et. al., was followed.^{11,12} To a stirred mixture of 45 g (0.5 mole) of p-chloraniline (Eastman Chemical) in 2 l of benzene was added 125 g (0.5 mole) lead dioxide (Eastman, Celvan, and Mills). The mixture was stirred for 2-3 hours after which the mixture was refluxed for 2-4 hours. The cooled suspension was filtered and 125 ml concentrated hydrochloric acid added to precipitate the solid

acid from the mixture. The aqueous portion was collected by filtration and dissolved in 300 ml of water. The pH was adjusted to 8.0 with concentrated sodium hydroxide. The green suspension was then extracted with methylene chloride with some difficulty, using 500 ml portions until an aqueous color was obtained in the new methylene chloride layer. The combined portions of methylene chloride were then dried with magnesium sulfate and filtered. The organic solvent was removed from the filtrate leaving a dark brownish-orange solid. This solid proved to be a mixture of several components which simple recrystallization could not separate. The benzene soluble portion of the solid was taken up in a minimum amount of benzene and columned with benzene through a large (18 in x 12 in) column filled with 60-80 mesh silica gel (Rohm and Haas, Columbus, and Bell). Removal of the benzene from the middle fraction left the pure compound, which was very bright red orange in color. The other components were not characterized.

Yield 10 g-21.4 g (23-25%); m.p. 110-114°C;

lit. m.p. 110-112°C.¹¹

2,4-Pyridinedicarboxylic-This compound was prepared by the reduction of the 8-ethyl ester of 2,4-pyridine dicarboxylic acid with lithium aluminum hydride by the method of Jones and Kornfield¹² or used as purchased from Aldrich Chemical Co.

2,4-Pyridinedicarboxylic-A modification of the method of Papadopoulos, et al.¹³ was employed. Sixty grams of freshly prepared manganese dioxide¹⁴ was suspended in 100 ml

of chloroform (approx. 500 ml) to 1,4-dioxane/ether, the mixture was stirred at room temp. for 3 hours, filtered, and the solid washed with 100-200 ml portions of ether. The filtrates were combined and concentrated under reduced pressure. The residue was taken up in a minimum amount of a mixture 80% benzene and 20% ethylacetate. This was placed on a silica gel (40-100 mesh, Matheson, Coleman, and Bell) column and eluted with the same mixture collecting the middle portion (400 ml) after discarding the first 70-100 ml. The desired fraction was reduced in volume to 10 ml and the solution was placed in a refrigerator over night. The white crystals were collected by suction filtration and washed twice with benzene.

Yield: 1.5 g (45%); m.p. 122.5-124.5°C;

lit. m.p. 124°C.¹¹

1,4-Pyridinediacetylpyridones-8 modification of the

procedure of Carey, et al.¹¹ was followed. Five grams (12.1 mmol) of 1,4-diacetylpyridine was dissolved in 100 ml absolute ethanol and this solution added dropwise to a stirred solution of 10-12 g 40% hydrazine (Matheson, Coleman, and Bell) kept at 15°C. Stirring was continued overnight as the temperature slowly increased to room temperature. The crude product was collected as a saturated glass foam and recrystallized from absolute ethanol. Repeated attempts to purify the product by recrystallization were unable to lower the m.p. to the reported value of 181°C.¹¹ However, only one component was shown by thin layer chromatography using various eluents.

Yield: 5.1 g (45%); m.p. 145-150°C; lit. m.p. 180°C.¹¹

1,2-Diphenyl-3-methyl-4-nitro-5-oxo-1,2,3,4-tetrahydronaphthalene—A modification of the method reported by Fischer and Smith¹¹ was followed. Two grams of 1,2-diphenyl-3-methyl-4-nitro-5-oxo-1,2,3,4-tetrahydronaphthalene (0.015 mole) in 10 ml. of absolute ethanol was added dropwise with stirring to an excess of 4% hydrazine (Matheson, Coleman, and Bell) which had been diluted with approximately 10 ml. absolute ethanol. Stirring was continued for fifteen minutes and the solution placed in the refrigerator overnight. A few crystals had formed by the next morning. However, to ensure complete reaction, the solution was warmed and stirred for an additional 4 hours at approximately 35-40°C. It was then cooled to 0°C. and 5% aqueous, well-formed crystals were collected and washed with cold absolute ethanol on the sintered glass funnel. Recrystallization from absolute ethanol, yielded a product with only one component as indicated by thin layer chromatography, but again with a melting point slightly higher than that previously reported.

Yield: 1.1 g (78%); m.p. 143-45°C; lit. m.p. 133-135°C.¹¹

1,2-Diphenyl-3-methyl-4-nitro-5-oxo-1,2,3,4-tetrahydronaphthalene—This compound was prepared by a modification of the method of Fischer and Smith.¹¹ Thirty-one ml (0.25 mole) of approximately 4% aqueous glyoxal (Fisher Scientific Co.) was added dropwise from a separatory funnel into a 250-ml. beaker submerged in an ice bath and equipped with a magnetic stirrer. The beaker contained 75 ml (0.25 moles) of a solution of 4% aqueous hydrazine (Matheson, Coleman, and Bell) which was stirred continuously throughout the addition. No precipitate was observed immediately on

stirred in the refrigerator. Stirring was continued for another 3 hours as the temperature gradually increased to room temperature because the ice surrounding the beaker was allowed to melt. The solution was then placed in the refrigerator overnight. Removal of the beaker showed only traces of a precipitate, so the solution was placed on the rotary evaporator and the volume reduced from ~125 ml to 50 ml. An off-white colored solid was observed and the slurry was transferred to a distilled glass funnel and filtered. The filtrate was orange-yellow and the crystals were light yellow and washed with 10 ml of H₂O followed by ~10 ml of 5% ethanol followed which the product was white. The solid was placed in a vacuum desiccator and dried in vacuo over Drierite. Care was taken to protect the reaction mixture and the crystals (especially while damp) from the light as yellow discoloration appeared rapidly.

Yield: 10.8 g (38%), m.p. 33-33.5°C,

lit. m.p. 33-33°C. ¹⁴

Glucosylidihydrazine-A procedure similar to the glycosylidihydrazine preparation was followed. One hundred twenty-five ml (2.5 moles) of 64% aqueous hydrazine (Fisher, Coleman, and Weil) was placed in a 250 ml beaker immersed in an ice bath. To this was added dropwise 53 ml (0.5 mole) of bisacetyl (Fisher Scientific Co.) while the resulting solution was stirred. A white solid formed and became so voluminous that extensive mixing of the additional bisacetyl became impracticable and the latter portion remained as a yellow

light yellow. The clear red film fused with 5 ml. benz. The clear solution was cooled to 0°C. The yellow precipitate washed with 1.0 ml. ethanol and was removed the yellow coloration. The 50 mg (1/2) sparing solubility in H₂O or ethanol, the solid was dissolved in warm DMS containing acetic acid and refiltered. The light yellow solution was cooled producing a white precipitate which was collected by filtration and washed with a small portion of DMS followed by 2 portions of ethanol.

Yield: 25 g (55%). m.p. 155-156°C; lit. m.p. 151°C.¹¹

2,6-Diacetylpyridine-This was purchased from Aldrich Chemical Co. and recrystallized from 25-30° petroleum ether. m.p. 75-80°C.

2-Acetyl-3-oxo-2,6-dimethylpyridine-Similar procedures to those of Sauerbrey, et al.,¹¹ were followed in this preparation. Commercially available 2-acetylbenzalddehyde (Aldrich Chemical Co.) was dissolved in 250 ml of absolute ethanol to which 25 drops of concentrated hydrochloric acid and 3.75 g anhydrous calcium chloride (Fisher Scientific Co., 4 mesh) was added. The mixture was placed in a desiccator over anhydrous calcium chloride and out of contact light for 7 days. It was then neutralized to pH 7.5 with sodium methoxide (Mallinckrodt Chemical Works) in methanol. The solution deepened as yellow color as pH 7.5 was reached. The clear solution was placed on the rotary evaporator to remove the solvent. After only slight volume reduction, an oily "mass" began to appear. The flask was removed and 150 ml of vinyl ether was added followed by 100 ml of water. The water layer was

condensed in a vacuum flask and collected (140 g) and was 181 g of oil. The 220 g of oil was combined and placed in the rotary evaporator. In 10 min the solvent was removed. The resulting oily mass (130 g) was distilled using boiling chips at a pressure of 1.5 mm with the distillate collected in the range 114.5-118.5°C. Nearly all of the material distilled within this range yielding a yellow-green oil.

Platinum dioxide—This compound was either prepared by the method of Adams, *et al.*,¹³ or purchased from Matheson, Culman, and Bell.

Hydrogenation of 6-methyl-2-octadecylnon-6-ynal—Hydrogenation of previously prepared 6-methyl-2-octadecylnon-6-ynal was attempted using an apparatus prepared by Dr. David Schindler in this laboratory. Approximately 25 g of platinum dioxide was placed with 15 ml of methanol in the reaction chamber, stirred vigorously while the chamber was flushed 3 times with nitrogen, and then filled with hydrogen. Hydrogen uptake was allowed to proceed until no longer evident. The 6-methyl-2-octadecylnon-6-ynal (18.66 g, 0.166 mol) and an 18 ml absolute methanol was added through a side arm with care being taken not to introduce any oxygen. The stirred mixture was allowed to react for 18 hours consuming an excess of 5.1 percent of the calculated volume of hydrogen required. After hydrogen uptake had ceased, the system was evacuated and flushed 4 times with nitrogen. The mixture was removed and the platinum catalyst removed by filtration. The filtrate was then transferred to a 100 ml round-bottom flask fitted

via aried, 100 ml flask to a 500 ml trap and placed on a rotary evaporator to remove the solvent. The oil which remained after 15 minutes was flask to 40°C in vacuo was collected, the yield being 100% (14.8 g) of the theoretical. The crude product as collected showed an appropriate IR spectrum but integration of the NMR proton chromatogram was slightly low. Attempted distillation of the crude product under reduced pressure decomposed the compound so the oil was used directly without further purification.

Hydroxylation—This compound was prepared with assistance from a cooperation with Dr. Wm. Gilroy following the method of Fieser and Beer.¹¹⁰ A second method suggested by Dr. J. A. Schooley¹¹¹ involved the preparation of acrolein acetal,¹¹² formation of the epoxide following the method of Emmons and Favors¹¹³ and then cleaving the epoxide with periodic acid using the procedure of Fieser and MacBarrat,¹¹⁴ neither method was successful in producing quantities sufficient for further study.

Allyl Hydroxymercuration—This compound was graciously provided by Dr. Frank A. Jelen who used the method of Fieser and Beer¹¹⁵ to prepare the material.

Reaction—Five ml of 50% hydrogen (2.37 mmole) was added dropwise with rapid stirring to a mixture of 48 g (0.48 mmole) benzoyl and 25 ml water cooled in an ice bath. After the formation of a yellowish color, 100 ml of water was added. The mixture became cloudy as the ice melted and after 15 minutes the mixture was clear. Further vacuum clarified the

solution and it was warmed to 70°C and stirred for 2 hours. The solution was placed in the refrigerator over night and white needle-shaped crystals were formed. These were filtered, pressed with filter paper and allowed to dry in a stream of dry nitrogen. The method of preparation is essentially that of Stratton and Sauer.¹¹

Yields 18 g (33%); M.P. $33-34^{\circ}\text{C}$, lit. m.p. $33-34^{\circ}\text{C}$.

Analysis for $\text{C}_8\text{H}_7\text{N}_3\text{O}_2$

Calculated: C, 57.35; H, 3.23; N, 14.75.

Found: C, 55.24; H, 3.75; N, 14.75.

Microscopic Crystal—Dr. Fodor also provided this compound having used a modification of a patent procedure¹² to prepare it.

Microscopic Crystal—The lengthy and sensitive method of Hudnott, et al.,¹³ was followed to prepare this compound. The product is now commercially available from Terra Marine Storesearch of California.

Formaldehyde Isomerase—A slurry of 10% paraformaldehyde (Fisher 241 in white mineral oil (b.p. $334-336^{\circ}\text{F}$) was heated to $115-120^{\circ}\text{C}$ and carried by a stream of dry nitrogen over the reaction chamber. An alternative method is described by Faccio.¹²

Crystallization—The procedure described in Fieser¹⁴ was followed for recrystallization. The recrystallized product was unusually exposed to light while still damp. The product was dried overnight, in vacuo and kept in a dark

factor. The procedure used would result in less than 100% recovery of the sample.

Procedure

Analysis of the sample—A portion of nickel and copper in various combinations prepared sample of the solid sample was placed in a 50 ml beaker in which was added ~50 ml of a 1:1 mixture of concentrated nitric and perchloric acids. This was digested to almost dryness on a hotplate and diluted to ~50 ml with water, taking care to wash the digesting beaker very thoroughly. The pH of the resulting solution was then raised as it by adding of a 10% sodium hydroxide. A known volume of 0.0100 N disodium ethylenediaminetetraacetate (Fisher Scientific) was added in excess of that required to complex all available nickel(II). Two or three drops of a solution of Eriochrome Black T (E.T. Fisher Chemical Co.) was then added as an indicator. Then the mixture was titrated with 0.01 N zinc(II) chloride solution which had previously been standardized against the EDTA solution to determine its exact concentration. This procedure allowed calculation of the amount of Ni(II) present based on the total amount of EDTA present initially and the amount of Ni(II) needed to complex the remaining EDTA not complexed by the Ni(II). The method is similar to that described by Flecken.^{2,3} A procedure identical to that used for nickel was followed for the analysis of copper except that murexide was used as the indicator.

Preparation of 10,10'-bis(2-pyridyl)-9,9'-b. solution of 0.100 g 10,10'-bis(2-pyridyl)-9,9'-b. dissolved in 40 ml of absolute ethanol

100 mg (0.0004 mole) of 1,2,3,4-tetrahydro-2H-1-benzopyran-2-one was added to a stirred solution (50 ml) of absolute ethanol and absolute ethyl acetate (10 ml) of sodium chloride hydrate (100 mg) (Fisher Chemical). An immediate color change from yellow to dark purple resulted upon the addition of the acid compound. The solution was kept at 55°C for 1 hour. When the solid present was collected by filtration as a saturated glass formed. The solid was washed two times with absolute ethanol and two times with diethyl ether. The solid was then dried overnight in a vacuum desiccator.

Yield: 8.13 g 88% theoretical

Analysis for: $C_{18}H_{15}BrO$ (261)

Calculated: C, 67.39; H, 3.63; Br, 18.98; O, 18.21.

Found: C, 68.35; H, 3.34; Br, 18.29; O, 18.81.

Preparation of 1,2,3,4-tetrahydro-2H-1-benzopyran-2-one A solution of 2.000 g (0.008 mole) of 1,2,3,4-tetrahydro-2H-1-benzopyran-2-one was added dropwise with stirring to a solution of anhydrous sodium bromide (0.14 g, 1.2 mmole from E. & E. Laboratories) dissolved in 150 ml absolute ethanol at 55°C. A color change to purple as well as the formation of a precipitate was immediate. The solution was continuously stirred for 4 hours while the temperature was maintained at 55°C. The solid was collected and washed as above and dried in a vacuum desiccator overnight.

Yield: 0.64 g 80% theoretical.

Analysis for: $C_{18}H_{15}BrO$ (261)

Calculated: C, 67.39; H, 3.63; Br, 18.98; O, 18.21.

Found: C, 68.35; H, 3.34; Br, 18.29; O, 18.81.

Preparation of NICKEL-GLUCONATE-The procedure outlined for the bromide preparation was followed using 150 ml of an absolute ethanol solution of nickel(II)nitrate hexahydrate (6.484 g, 2.3 mmole from J.T. Baker Chemical Co.) with the GLUCON (6.500 g, 2.3 mmole) in absolute ethanol being added slowly. The precipitate was collected and collected as above and dried in vacuo overnight.

Yield: 6.43 g 80% theoretical.

Analysis for: $NiC_{12}H_{22}O_{14}$

Calculated: C, 43.42; H, 3.34; Ni, 21.60; H₂O, 17.48.

Found: C, 43.53; H, 3.49; Ni, 21.68; H₂O, 17.41.

Preparation of NICKEL-GLUCONATE-Following the procedure used for the bromide complex above, anhydrous nickel(II)nitrate (3.418 g, 2.3 mmole from E. I. Laboratories) in 150 ml absolute ethanol and 150 ml absolute ethanol solution of GLUCON (6.500 g, 2.3 mmole) added slowly with stirring. The precipitate which formed in the blue solution was digested and collected as above, then dried in vacuo.

Yield: 8.45 g 48% theoretical

Analysis for: $NiC_{12}H_{22}O_{14}$

Calculated: C, 47.60; H, 3.34; Ni, 21.60; H₂O, 17.48.

Found: C, 47.43; H, 3.29; Ni, 21.60; H₂O, 17.41.

Preparation of NICKEL-GLUCONATE-NICKEL-GLUCONATE-The procedure for the bromide preparation was followed using 6.500 g (2.3 mmole) nickel(II)nitrate hexahydrate (E.I. Laboratories) and 6.500 g (2.3 mmole) GLUCON. Collection and handling of precipitate was the same as above. The solid was extremely sticky as

to nitric acid and the compound is dissolved in the minimum amount of nitric acid.

Yield: 0.42 g 51% theoretical.

Analysis for $\text{Ni}(\text{C}_2\text{H}_5\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$

Calculated: C, 31.31; H, 4.39; Ni, 17.80; O, 45.50.

Found: C, 31.18; H, 4.33; Ni, 17.70; O, 45.18.

Preparation of $[\text{Co}(\text{NOOCH}_2\text{CH}_3)_2\text{Cl}]$ —This compound was prepared using the method described above for $[\text{Ni}(\text{NOOCH}_2\text{CH}_3)_2\text{Cl}]$. Copper chloride dihydrate in the amount of 1.125 g (3.3 mmole) was used along with 4.500 g (3.3 mmole) NOOCH₂CH₃. Collection and treatment was the same as for the nickel complex.

Yield: 0.50 g 78% theoretical.

Analysis for: $\text{Co}(\text{C}_2\text{H}_5\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$

Calculated: C, 44.35; H, 7.97; Ni, 18.86; Co, 28.78.

Found: C, 44.70; H, 7.43; Ni, 17.82; Co, 28.37.

Preparation of $[\text{Co}(\text{NOOCH}_2\text{CH}_3)_2\text{Cl}]$ —Preparation and collection was effected by following the same method as for the chloride complex using 0.548 g (3.3 mmole) of copper nitrate trihydrate and 0.500 g (3.3 mmole) NOOCH₂CH₃.

Yield: 0.38 g 65% theoretical.

Analysis for: $\text{Co}(\text{C}_2\text{H}_5\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$

Calculated: C, 44.35; H, 7.97; Ni, 18.86; Co, 28.78.

Found: C, 43.80; H, 7.31; Ni, 18.74; Co, 28.70.

Preparation of $[\text{Co}(\text{acacatoacetate})_2\text{Cl}]$ by the "template reaction"—The nickelous chloride hexahydrate (Riedel Chemical) and the 2,4-diacetylpyridone (Aldrich Chemical, recrystallized from petroleum ether) were dissolved in approximately 100 ml

of absolute ethanol in the amounts of 2.495 g (0.0815 mole) and 1.105 g (0.0815 mole) respectively and placed in a 250 ml round-bottom three-necked flask equipped with a magnetic stir bar. This solution, light yellow in color, was brought to reflux and then four drops of concentrated hydrochloric acid were added. This was followed by dropwise addition from a 125 ml separatory funnel connected by ground glass joints of 0.482 g (0.0815 mole) cobalt dissolved in approximately 100 ml of absolute ethanol. This mixture, which turned a purple color on addition of the new compound, was refluxed for some hours and filtered hot through a fine sintered glass filter; the small amount of solid separated was discarded. The brown filtrate was placed in a 200 ml beaker and stirred with a magnetic stir bar while approximately 100 ml diethyl ether was added dropwise from a separatory funnel. The brownish purple solid produced was collected on a medium sintered glass filter taking care to not let the solid complex be exposed to the atmosphere until dry. When the surface of the filtrate just reached the solid in the filter, suction was removed and about 20 ml diethyl ether added and redried with the solid on the filter, then the suction was replaced and the surface level brought to the top of the solid. This process was repeated two more times. On the third ether wash, a funnel backed to the line nitrogen source was placed over the filter and after the ether was removed by suction through the filter bed, the nitrogen stream dried the complex on the filter. If these steps were not followed, the complex would become very gummy and dark brown-black in color. The solid was then dried in vacuo for 12 hours.

melting 8.75 g 84% theoretical with the percent yield on other preparations ranging from 48 to 45%.

ANALYSIS FOR $\text{NiOCl}_2 \cdot 6\text{H}_2\text{O} \cdot \text{HCl}$

calculated: C, 53.78; H, 5.54; Ni, 14.93; Cl, 12.82

found: C, 53.44; H, 5.75; Ni, 14.83; Cl, 12.47

These figures represent an average of five analyses on five independently prepared samples. The precision was 0.12, 0.15, 0.23, and 0.28 for carbon, hydrogen, nitrogen and nickel respectively.

Preparation of $\text{Ni}(\text{acetylacetonate})_2\text{HCl}$ by the "delay reaction"

The order of addition for the starting materials is the major change from the previous preparation. The 2,4-diacetyl-2-pyridone (Gibbs Chemical, recrystallized) and COMAB in the amounts of 8.2754 g (0.0048 mole) and 6.1113 g (0.0048 mole), respectively, were added as solids to a 125 ml 3-necked round-bottom flask equipped with a magnetic stir bar and condenser. The flask contained approximately 85 ml absolute ethanol at reflux and 2 to 3 drops of concentrated hydrochloric acid were added immediately after addition of the ketone and are compounds. This solution was kept at reflux for three minutes after which time 6.1113 g (0.0048 mole) of nickel(II)chloride hexahydrate dissolved in about 25 ml absolute ethanol was added all at once. The refluxing was continued for 26 hours after which the product was collected in an identical manner to that described under the "template reaction" preparation. The product yielded an identical

1-ethyl-3-(3-dimethylaminopropyl) carbodiimide prepared by the "Bertozzi" method;

Yield: 5.17 g 84% conversion;

Analysis for: $C_{11}H_{14}N_2O_2$

Calculated: 84, 13.84

Found: 84, 13.84

Preparation of [Ni(methylamino)₂Cl₂] using [Ni(COAAH-2)Cl₂]

as a starting material--Previously prepared [Ni(COAAH-2)Cl₂] (8.888 g, 0.0388 mole) was added as a solid to approximately 88 ml of refluxing absolute ethanol in a 125 ml 3-necked round-bottom flask equipped with a magnetic stir bar and condenser. Immediately after the addition of the complex, 8.188 g (0.0388 mole) of 2,4-diacetylpyridine was added as well as 2 ml of drops of concentrated hydrochloric acid. The initial purple color changed fairly rapidly to brown a characteristic color of the merocyclo. Reflux was continued for 18 hours after which the product was collected in a similar fashion to the previous two preparations.

Yield: 6.15 g 81% theoretical.

Analysis for: $C_{11}H_{14}N_2O_2$

Calculated: 84, 13.84

Found: 84, 13.84

Preparation of [Ni(methylamino)₂Cl₂] by the "Bertozzi"

method--Nickelous chloride hexahydrate, 6.948 g (0.0388 mole) and 8.848 g (0.0388 mole) 2,4-pyridinedialdehyde were dissolved in approximately 800 ml absolute ethanol at 75°C contained in a 1.5 liter 3-necked round bottom flask equipped with a magnetic stir bar and condenser. The temperature was then

lowered to 41.1°C and 0.0457 g (0.004 mole) SOCl_2 dissolved in approximately 100 ml of absolute ethanol at room temperature was added dropwise over a period of 14 hours. The solution turned the familiar purple color of the $[\text{Ni}(\text{SO}_4\text{NH}_2)_2\text{Cl}_2]$ complex upon addition of the first few drops of the SOCl_2 solution but soon turned to the brown color similar to that of the anhydrous complex. The solution was kept at $43-45^{\circ}\text{C}$ for 12 hours and then was reduced in volume to about 450 ml using a water separator. The heating controls were not altered, thus the temperature was maintained at approximately room temperature even with the evaporation procedure. The volume reduction took three hours at which time the product was forced out of solution by slow addition of 100 ml diethyl ether and then collected in a flask the same as in the $[\text{Ni}(\text{acetylacetonate})_2\text{Cl}_2]$ preparation. After producing the nitrogen dried complex, the solid from this preparation was placed in a vacuum oven at 18°C over P_2O_5 in vacuo for a period of eight to twelve hours.

Yield: 4.72 g 48% theoretical.

Analysis for: $\text{NiC}_{12}\text{H}_{18}\text{N}_2\text{OCl}_2$

Calculated: C, 51.78, H, 3.97, N, 15.89, Ni, 15.31

Found: C, 51.78, H, 3.11, N, 15.97, Ni, 15.15.

These values represent an average of three analyses on three independently prepared samples. The precision was .17, .08, and .17 for the carbon, hydrogen and nitrogen respectively.

Preparation of $[\text{Ni}(\text{acetylacetonate})_2\text{Cl}_2]$ -nickel(II)chloride hexahydrate to the extent of 0.031 g (0.0040 mole) plus

(100) 1.0000 g of 1,2-dichloroethane was dissolved
 in 100 ml of absolute ethanol. The solution was added to
 100 ml of 1,2-dichloroethane. A solution of 0.715 g (0.00333
 mole) 1,2-dichloroethane in 100 ml of warm
 absolute ethanol (95%) was added dropwise with stirring
 through a separating funnel. The mixture was refluxed for
 an additional two hours. A water aspirator vacuum was hooked
 to the apparatus to remove part of the solvent. The solution
 attained an equilibrium temperature of approximately 60°
 while the solvent was reduced to a volume of 100 ml. The
 solution was kept at 45°C for an additional two hours and
 then filtered in a manner similar to the (bromochloroacetyl)₂.
 The nitrogen dried sample was then placed in a desiccator
 for 24 hours.

Yield: 0.48 g 2% theoretical

Analysis for: $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2$

Calculated: C, 48.28; H, 4.85; N, 18.78; O, 18.10,

Found: C, 48.22; H, 4.92; N, 18.56; O, 18.10,

100

The anomalous, temperature-independent magnetic moments are 1.10 and 2.10 B.M. for Fe^{2+} and V^{3+} , respectively. The complex Fe^{2+} was shown to follow unequivocally the Curie-Weiss

For ligands 1 and 2, the $\chi_{\text{M}}^{\text{Mn}}(\text{O})$ and $\chi_{\text{Mn}}^{\text{Mn}}(\text{O})$ values for the same range exhibit a slight deviation in the $(1/\chi_{\text{M}}^{\text{Mn}})^{-1}$ versus T plot within the region 100°-300°K. The only other characteristic in which the two structurally related complexes differed significantly is their ultraviolet-visible spectra. These differences in the temperature-dependent magnetic susceptibilities and the spectra mentioned may reflect slight structural differences which Framework Molecular Models predict, could be caused by steric interactions resulting in a slight puckering of the basic macrocyclic ring of the complex (vii). Both complexes exhibit thermal stability to 300°C and can withstand contact of concentrated mineral acid at elevated temperatures for periods of several hours, a characteristic reported for other macrocyclic complexes.

A third macrocycle, 2,5,11,14-tetraazacyclododecane-10-hexamethylenediamine-11,1,1,1- 10^{-10} (chromyl-1190)-2,5,8,8,10-(Hf), 11,11,13,13,17-tetraazabicyclo(11,11,11)triazole (PVI), was prepared and characterized by elemental analysis and infrared spectral and room temperature magnetic susceptibility measurements. Numerous attempts to prepare two closely related complexes, (VII) and (VII), were unsuccessful. However, the preparation of the basic macrocycle obtained above opens an interesting and new area of research in macrocyclic complexes concerning nitrogen-nitrogen bonds.

A series of complexes [M(MDAAB-R)] have been prepared and characterized where M = Yb(III) or Ce(III), and R = Cl⁻, Br⁻, SCN⁻, NO₂⁻ or CNO⁻ and [MDAAB-R] = the tridentate

ligated boron nitride was used as such. Both the B_2N_2 and B_3N_3 were characterized by infrared, ultraviolet and visible spectra, magnetic susceptibilities, accurate molecular weights and elemental analysis. The data collected are entirely consistent with a formulation of these complexes as neutral, square-planar species. This series of complexes should provide a convenient starting material for the preparation of macrocyclic ligands containing the nitrogen-nitrogen double bond.

APPEAL



I

Porphyrin skeleton



IIa

Corrin skeleton



IIb

Pthalocyanine skeleton



III

Cholate rings

a = 5 member cholate ring
b = 6 member cholate ring

12



- a) $R_1=R_2=H$, glymesol
- b) $R_1=R_2=CH_3$, bisacetyl
- c) $R_1=H$, $R_2=CH_3$, pyrimidolacetyl
- d) $R_1=H$, $R_2=H$, bispyrimidol
- e) $R_1=H$, $R_2=H$, bisacetyl

7

, $2Cl^+$

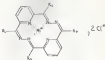
- a) $R_1=R_2=CH_3$, 4,12-dimethyl-1,11-dinitro-11g-dibenzog, g, [1,2,5,11]tetraazapentacyclopenta-
benzenesulfonyl chloride.

Abbreviated as [9] (acetone) Cl_2

- b) $R_1=R_2=H$, 7,11-dinitro-11g-dibenzog, g, [1,2,5,11]tetraazapentacyclopenta-
benzenesulfonyl chloride.

Abbreviated as [9] (acetone) Cl_2

(9)



- a) $R_1=R_2=R_3=R_4=\text{CH}_3$; 1,3,9,10-tetramethyl-2,4,6,8,12,16,20-hexamethylcyclo[12]pentaene-1,11,13,15-tetrakis(1,10,12,14,16,17-hexamethyl[21]chloride)

Abbreviated as [25] (xix) (xix) (xix) (Cl)₄].

- b) $R_1=R_2=R_3=R_4=\text{H}$; 2,4,12,13,16,18-hexamethylcyclo[12]pentaene-1,11,13,15-tetrakis(1,10,12,14,16,17-hexamethyl[21]chloride)

Abbreviated as [25] (xx) (xx) (xx) (Cl)₄].

- c) $R_1=R_2=\text{H}$, $R_3=R_4=\text{CH}_3$; 2,12-dimethyl-2,4,12,13,16,18-hexamethylcyclo[12]pentaene-1,11,13,15-tetrakis(1,10,12,14,16,17-hexamethyl[21]chloride)

Abbreviated as [25] (xi) (xi) (xi) (xi) (Cl)₄].



VII

$R_1 = R_2 = H$, reduced bisbenzophenone (CDBAAR)



VIII
28

VIII- $R_1 = R_2 = CH_3$ is 3,6-di-
acetylpyridine
28- $R_1 = R_2 = H$ is 3,6-acetyl-
pyridine (acetylpyridine)

29



IX

- $R_1 = R_2 = H$: 1,3-diacetyl-4-methyl-6-methylpyridine
- $R_1 = R_2 = CH_3$: 1,3-diacetyl-4-methyl-6-methylpyridine



X

(CDBAAR-21C)

4-III(2) or 6-III(2)

$R_1 = H$, $R_2 = H$, $R_3 = H$, $R_4 = H$
or CH_3

^a There will be no structure corresponding to this roman numeral in order to avoid confusion with the sales symbol.



XXIII

9603



XXIV

9604



XXV

2,4-pyridinedicarboxylic acid



XXVI

2,4-pyridinedicarboxylic acid



XXII

1,1-dichloropropane



XXIII

triethylorthoformate



XIX



XX



XXI



XXII

- a) $R_1 = R_2 = CH_3$
- b) $R_1 = CH_3$, $R_2 = CH_2$



XXIII

- a) $R_1 = R_2 = H$, glyoxalaldolacetone
 b) $R_1 = CH_3$, 3-methylaldolacetone
 c) $R_1 = R_2 = C_2H_5$, 3-pentaldolacetone



XXIV



XXV

α-phenylacetaldolone



XXVI



XXVII



XXVIII

- a) $R_1 = R_2 = H$, glyoxalacetaldol
 b) $R_1 = R_2 = CH_3$, 3-methylacetaldol



10010



p-oxipolymethylol

b) EtOH , 1-oxipolymethylol-
hydroxyethylolc) EtOH , 1-oxipolymethylol-
dimethylol

10012



10013



10014

6-oxipolymethylol
(10014)

10015



2077



2007

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BIOGRAPHICAL SKETCH

Stanley Reed Meller was born September 14, 1914, at Mishawaka, Indiana. In June, 1932 he was graduated from Manchester High School in North Manchester, Indiana. In June, 1934 he was awarded the degree of Bachelor of Science from Manchester College with a major in chemistry and a minor in physics. In September of 1934, he enrolled in the Graduate School of the University of Florida. He worked as a graduate assistant in the department of Chemistry until June, 1937. From June until September of 1937, he left the University of Florida to work in industry at Eli Lilly and Co., Indianapolis, Indiana. In September, 1937 he returned to the University of Florida and was supported by a National Science Foundation Grant until December 1943. During this time period he volunteered for several teaching assignments in the Department of Chemistry. From January 1943 until April 30, 1949, he was appointed as a teaching assistant and then was supported as war funds from May 1, 1949 until March 31, 1950. He was supported duty free from April 1 until August 31, 1950. In September, 1950 he started teaching full time in the chemistry department of Manchester College where he is still employed.

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